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Licenciada em Conservação-Restauro

Challenges in the conservation of historical chemicals: Corrosion patterns in glass containers and development of preservation guidelines

Dissertação para obtenção do Grau de Mestre em
Conservação e Restauro, especialização em Conservação e Restauro

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“One never notices what has been done; one can only see what remains to be done.”
- Marie Skłodowska Curie (1894)

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Abstract

Collections of chemicals are assemblies of substances associated to chemical operations. These collections often have a large historical significance and can be found in departments, research institutions, schools or other spaces. So far, seldom dedicated studies have been made, both to the materiality of these collections, as well as for their conservation.

For this dissertation, the glass containers in the collection of historical chemicals from the National Museum of Natural History and Science from the University of Lisbon (MUHNAC) are studied, as they are the largest storage material found in the collection and present signs of active deterioration, in the form of corrosion patterns. This research followed a three-fold approach – a collection survey was performed to assess the collection's dimension; followed by a full conservation assessment of the corrosion patterns, collection locations and environmental conditions and the establishment of the conservation condition for the collections' glasses. Lastly, an analytical approach was taken. Glass surface measurements indicate the alkalinisation of the glasses, as a sign of active corrosion. Through the use of *in situ* p-XRF analyses, glass chemical composition groups are correspondent with soda-lime-silicate glasses. Samples of aqueous chemical solutions were also collected and analysed through ICP-AES and HPIC with the goal to determine if the chemicals matched the containers' labels and if they may present glass dissolution products.

One of the outcomes of this dissertation is the development of preservation guidelines, through the empirical and analytical data gathered from the study of the MUHNAC's collection, as well as the results of a survey addressed to similar institutions holding historical collections of chemicals. The final result is the proposal of guidelines that outline selection criteria for chemicals, tools and measures for collections' care to objects and actions for collections' keepers. It is intended that these guidelines may aid small and large institutions in the preservation of their collections.

Keywords: Scientific Heritage; Collections of historical chemicals; Glass corrosion patterns; 19th century glass; Conservation assessment; Preservation guidelines.

Resumo

As coleções de reagentes são conjuntos de substâncias associadas a operações químicas. Estas coleções possuem uma vasta significância histórica e podem ser encontradas em departamentos universitários, instituições de investigação, escolas ou outros espaços. Até à data, poucos estudos foram realizados quer sobre a materialidade destas coleções, quer sobre a sua conservação.

No contexto da presente dissertação, os frascos de vidro presentes na coleção histórica de reagentes do Museu Nacional de História Natural e da Ciência da Universidade de Lisboa (MUHNAC) é estudada. O vidro é o material de armazenamento de maior presença na coleção e é aquele que apresenta maiores sinais de deterioração ativa, sob a forma de padrões de corrosão. Esta investigação possui uma abordagem em três partes – um levantamento da coleção foi realizado para determinar as dimensões da coleção; seguida de uma avaliação de conservação dos padrões de corrosão, dos espaços da coleção e das condições ambientais dos mesmos e a determinação de uma escala de estado de conservação para os vidros da coleção. Por fim, é efetuada uma abordagem analítica. Medições superficiais das superfícies dos vidros indicam a alcalinização dos mesmos, indicando sinais de corrosão ativa. Através do uso de p-XRF *in situ*, são determinados grupos composicionais que correspondem com vidros sodocálcicos. Amostras de reagentes aquosos foram recolhidos e analisados através de ICP-AES e HPIC com o objetivo de determinar se os reagentes correspondem às etiquetas dos seus frascos e se é possível identificar produtos de dissolução do vidro.

Um dos resultados desta dissertação é o desenvolvimento de diretrizes de preservação, através dos dados empíricos e analíticos obtidos do estudo da coleção do MUHNAC, bem como dos resultados de um questionário direcionado a instituições que possuam coleções históricas de reagentes. O resultado final é a proposta de diretrizes que delineiam critérios de seleção para reagentes, medidas para o cuidado de coleções e ações para os responsáveis das mesmas. Pretende-se que estas diretrizes possam auxiliar pequenas e grandes instituições na preservação das suas coleções.

Palavras-chave: Património científico; Coleções históricas de reagentes; Padrões de corrosão em vidro; Vidro do séc. XIX; Avaliação de conservação; Diretrizes de preservação

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Symbols, Acronyms and Abbreviations

CMoG	Corning Museum of Glass
FCUL	Faculty of Science of the University of Lisbon
FMUL	Faculty of Medicine of the University of Lisbon
HPIC	High Performance Ionic Chromatography
HVAC	Heating, Ventilation and Air Conditioning systems
ICOM-UMAC	International Council of Museums – Committee for University Museums and Collections
ICP-AES	Inductively Coupled Plasma – Atomic Emission Spectrometry
ICM	Portuguese Institute for Conservation and Museums
IICT	Tropical Research Institute
IDL	Classical Meteorological Station of the Instituto Dom Luiz
IR	Infrared radiation
LPS	Lisbon Polytechnic School
MSDS	Material Safety Data Sheet
MUHNAC	National Museum of Natural History and Science of the University of Lisbon
OSHA	Occupational Safety and Health Administration
PCA	Principal Component Analysis
PPE	Personal Protection Equipment
p-XRF	Portable Handheld X-Ray Fluorescence
REACH	European union agency for Registration, Evaluation, Authorization and Restriction of Chemicals
UV	Ultraviolet radiation
VOC	Volatile Organic Compounds
μW/lm	Micro watt per lumen (unit for UV radiation measurement)
μA	Micro Ampere
kV	Kilo Volt
Lux	Unit for illuminance measurement
mg/L	Milligrams per liter
ppm	Parts per million
RH (%)	Relative humidity (in percentage)
T (°C)	Temperature (in degrees Celsius)
wt%	Weight percent

1. Introduction

Chemical collections are assemblies of substances that can either be found in nature, or obtained through chemical operations, such as extractions or synthesis and replicated as needed, therefore considered as artificial ^[1]. They can be found in the majority of research and educational contexts, often considered unsystematic collections, particularly when compared to those from natural history – which are arranged to demonstrate diversity in the natural world ^[1]. These substances can have a large significance both from industrial and historical perspectives (as is the case of collections of dyes) ^[1], but they are also material evidence of scientific practices, purposes and history within institutions.

The objectives of the present dissertation are the development of a comprehensive assessment of the collection of historical chemicals from the National Museum of Natural History and Science of the University of Lisbon (MUHNAC) and its focus on the collection's glass containers conservation condition ¹. To achieve this goal, a three-fold approach was followed: the first phase was the conduction of the survey of the MUHNAC's collection, mainly to comprehend what exists and where, which can be found in Chapter 1; followed by a second phase dedicated to the conduction of a conservation assessment, and third and final phase, with the analytical characterization of specific case studies within the glass containers. These can be both found in Chapter 3. This multidisciplinary approach aims towards the understanding of intrinsic and extrinsic factors and how they may interact with the present collections' material stability.

The typology of the collection studied represents a true challenge to the Conservation and Restoration field, since the few studies undertaken with a similar thematic have been mostly concerned with collections' hazards and safety, and less with their preservation and as scientific heritage. On this concern, the need to develop preservation guidelines for historical chemicals seemed paramount. This is an outcome of this dissertation, as institutions responsible for similar heritage may find these orientations useful, including for the improvement of their collections long-term preservation. The proposed guidelines can be found in Chapter 4.

1.1. Scientific heritage: definition and brief review on conservation challenges

Scientific heritage is a field which is in need of larger development both in terms of legislation, procedures and policies, and of methodologies for studies and guidelines for its preservation and accessibility ^[3]. Before briefly describing the particular problematics of this type of heritage and how these are challenging the conservation field nowadays, it is important to provide a definition for this specific heritage. The first challenge lies in the difficulty of establishing a clear definition, as scientific heritage “*mirrors the diversity (...) and complexity of science itself*” ^[3]. The definition adopted in the context of this dissertation reads as follows:

“Scientific heritage is the shared collective legacy of the scientific community, in other words, what the scientific community as a whole perceives as its identity, worth being passed on to the next generation of scientists and to the general public as well. It includes what we know about life, nature and the universe, but also how we know it. Its media are both material and immaterial. It encompasses artefacts and specimens, but also laboratories, observatories, landscapes, gardens, collections, savoir faire, research and teaching practices and ethics, documents and books” ^[3].

¹ The broader term ‘container’ is employed in this dissertation, as multiple morphologies of glasses can be found in the collection studied. However, none of the typical terms used as jar, bottle or vial seems to be appropriate for this case study, as they reflect different shapes and morphologies of glass containers. This is also the term most often employed in the descriptions of glass in industrial production for storage of substances ^[2].

This type of heritage is diverse in terms of materials, dimension, shape, contexts and provenances. They represent more than mobile objects assembled in collections. They may be found in the form of artefacts, specimens, small or large collections, stemming from multiple disciplinary areas of scientific knowledge – such as the natural and exact sciences, medicine, pharmacy, among others. It also can include natural heritage – such as botanic gardens –, or edified historical buildings associated with different research and educational purposes mirroring this aforesaid diversity ^[3-4].

It is often referred to scientific heritage – and particularly scientific collections –, as being found mostly outside museums ^[3-4], which as mentioned previously, can encompass other typologies of buildings without proper museological functions. But also, when they are preserved in schools, universities or other scientific institutions, that hold, accumulate and produce heritage of science for centuries, increasing this dynamic and challenging its preservation ^[4]. In this last context, these objects, collections and spaces could be frequently hard to perceive, but especially to protect and recognize as scientific heritage. The lack of visibility, variety on its dimension and dispersion, more often than not, can contribute to the risk of a silent and irreversible loss or damage ^[3-5].

Another characteristic of scientific collections, and an important point for the study of its context, is the fact that they can become frozen in time. If a collection is kept unused, or in addition, is coherently used and reused for a long period of time, but preserved in its original provenance and not dispersed, they can become a genuine “*time capsule*” of multiple knowledge ^[6].

Nonetheless, especially when abandoned of its main purpose, there may exist periods of latency where the collection or objects’ condition and its environment are unknown ^[6]. This could influence the later interpretation of these objects’ conservation, particularly at the moment of its preservation or musealization, which is a challenging issue for the conservation of scientific heritage. How much damage can be attributed to its use, regarding its maintenance routines or its absence? Its unknown history and latency periods, or the induced material deterioration, how can we measure them?

One point to consider is that the interest in the study and preservation of scientific collections is still recent and with less development than other areas of the cultural heritage. This is noted when taking into account the collection at study in the present dissertation, and the seldom studies that focus on collections of chemicals, or even in chemistry collections as a whole. It is important to recognize that more often scientific artefacts are being recognized as primary sources of information, especially in the context of the history of science, through the conception of object biographies ^[3-5], in which information is also of primary importance for their conservation and for conservators.

The central aspects for the aim of this study are the materials, its compositions and how they deteriorate and how they may interact in composite objects. – which is the case in chemicals, as they are not only composed by chemical substance, but also its container, labels or other constituents, such as lids, stoppers or sealants. These materials may not be compatible, or even manufactured with compositions that are less studied or that could contain toxic compounds ^[7] – an issue there is not totally new in scientific heritage ^[8-9]. This hazardous nature can be usually associated either to inherent hazards ² present in the material, from its innate nature – as in the case of chemicals –, or to acquired hazards, through the ageing and deterioration of materials, the objects’ use or contamination with other toxic or hazardous substances ^[8-9].

² A hazard is defined as “*the inherent property of a substance capable of causing harm*” due to chemical or physical characteristics such as toxicity, flammability, instability, radioactivity or explosive and reactive properties ^[10].

Due to the necessity to increase studies and knowledge on the materials found in scientific heritage, mainly to comprehend how they age and react with their environments, and what are their chemical or physical alterations^[7], there is an urgency in the further development of studies and the conservation of scientific heritage. This can be achieved through the characterization of its materials and assessing its conservation conditions and strategies for implementation of preservation measures. These contributions can provide guides for the long-term preservation of the historical values, materiality and traces that are useful for the construction of object biographies, as primary source of information for historians of science^[4], but also, to keep these collections for future generations.

1.2. The MUHNAC's collection of chemicals: historical context and survey

Located at the centre of Lisbon, the MUHNAC is a national museum accredited by the Portuguese Museums Network (RPM)³, under the direct administration of the University of Lisbon (ULisboa),^[11]. The museum holds nowadays around 3,5 million objects⁴, from both cultural and scientific significance, with the majority of its heritage dating from the 19th and 20th centuries^[11]. Its collections cover mainly the last 400 years of history of research and education from the previous institutions that gave origin to MUHNAC, but also from other institutions and provenances^[12-14]. Since 2015, the MUHNAC additionally comprises the preservation and management of the Tropical Research Institute's (IICT) edified natural heritage, and its collections⁵. The latter derives mainly from scientific expeditions conducted in the former Portuguese colonies during the 20th century^[15].

In total, its collections vary from a major diversity of natural history specimens, archaeological, ethnographic and scientific artefacts, to historical paper-based collections including, books, drawings, maps and manuscripts^[16]. Regarding the natural heritage and historical edified buildings, MUHNAC encompasses also under its management two botanic gardens – the Lisbon Botanic Garden, dating from 1878 and in Belém, the Tropical Botanic Garden, dating from 1906 –, and two historical astronomical observatories – the *Ajuda* Astronomical Observatory, from 1861 and the Polytechnic School Astronomical Observatory, from 1898^[16-17].

The history of the institutions that precede the museum is thick but very well documented, crossing paths with important historical institutions such as the Cotovia Novitiate, occupying the building from 1609 to 1759, and after, the Royal College of Nobles in 1761 until 1837, with the foundation of the Lisbon Polytechnic School (LPS). In 1911, with the establishment of University of Lisbon, the LPS is succeeded by the Faculty of Sciences of the University of Lisbon (FCUL) remaining in the same building^[18]. Nearly the end of the 20th century, the faculty partly survived a devastating fire in 1978, although with the loss of most of its natural history collections^[13, 19]. It was after this event, that the transfer of the Faculty of Sciences to the main pole of the university, in Campo Grande occurs, and the current building as we know nowadays as MUHNAC, is left to become a full dedicated university museum with the reorganization of its historical collections and with the increment of new ones^[17].

Within the MUHNAC's heritage diversity, there is a historical chemistry collection, which is composed by an assembly of scientific artefacts, stemming from the teaching and research contexts of chemistry, mainly from LPS and FCUL, containing around 3000 objects. The majority of the collection results from 150 years of continuous use and reuse in the aforementioned

³ Integrating the list of accredited museums by the RPM <<http://www.patrimoniocultural.gov.pt/pt/museus-e-monumentos/rede-portuguesa/m/museu-de-ciencia-da-universidade-de-lisboa/>> [Accessed September 2019].

⁴ Lourenço, M.C., personal communication, August 2019.

⁵ 'Decreto-Lei nº 141/2015 de 31 de Julho', *Diário da República* – 1ª série (148) (2015-07-31), 5185-5188.

institutions, until its musealization on the last quarter of the 20th century. The collection of chemicals is integrated in the MUHNAC's historical chemistry collection ^[20].

In order to fully understand the chemicals collection, a comprehensive survey was undertaken. Its aim was the assessment of the collection's dimension, its distribution within the museum's different locations, provenances and chemicals manufacturers, as well as the evaluation of other parameters, such as, the chemical's content found in the collection and the number of hazardous substances. This was achieved by through access to the museum's database ⁶, followed by a thorough validation of all individual items in the different museum locations.

The data compiled from this survey allows for a clear perception of the real dimension of the MUHNAC's collection of historical chemicals – encompassing presently, 1976 items. It is considered as an open collection, since the museum still incorporates historical chemicals, namely from its predecessor institutions, such those from FCUL/LPS, with the last entries being made in 2017 ⁷, or from other institutions recently integrated, as in the case of the IICT. Within this total, 1589 chemicals are stored inside glass containers, and thus, this group will be the object of the following study. Through the museum database, 82% of the collection can be digitally accessed, since it is minimally inventoried and has associated documentation.

Starting with the collection's dimension and distribution, this information has been compiled in Figure 1.1.

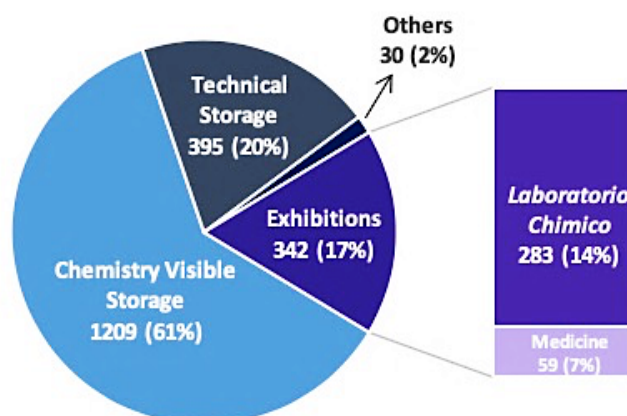


Figure 1.1. Distribution and dimension of the historical chemicals collection per museum locations.

A substantial part of the collection can be found in display at the Chemistry Visible Storage of the museum (totalizing 61% of the collection), with most of the historical chemicals stored inside a wooden four doors cabinet, that is still the original location of the chemicals as it was in the LPS in the 19th century ^[21] (Figure 1.2.). This location was restored and opened to the public in 2011, following the *Laboratorio Chimico* restoration (2003-2007), to become the new Chemistry Visible Storage, according to the museological plan for the reorganization of the historical chemistry collections, in a new concept of display, access and visibility ^[18, 21-22].

⁶ InPatrimonium © Sistemas do Futuro <<http://sistemasfuturo.pt/>>.

⁷ MUHNAC, 2017 (internal documentation)



Figure 1.2. The chemicals' cabinet in the Lisbon Polytechnic School (c. of 1880). Photographer: F. Rocchini. (Lisbon Municipal Archive – code PT/AMLSB/ROC/000084).

The second location with the largest quantity of historical chemicals, is the museum's Technical Storage of history of science (with 20% of the collection), which encompasses mainly chemicals from long term loans of other institutions, namely high schools.

The third location with further chemicals is the museum permanent and long-term exhibitions (with 17% of the collection) – divided into two locations. The first exhibition location, the *Laboratorio Chimico*, the original 19th century chemistry laboratory of the LPS. holds 14% of the historical collection of chemicals, stored in the laboratory former wooden cabinets. The second exhibition location, with 7% of the collection assessed, corresponds to the Medicine and Pharmacy collection presented at the, *Cuidar e Curar. A Medicina e os Museus da Universidade de Lisboa* exhibition, which is composed mainly by chemicals from the Faculty of Medicine of the University of Lisbon (FMUL) in the museum through a long-term loan since 2015 ⁸.

The remaining portion of the collection (2%), is distributed in other museum locations that are not open to the public or kept at the museum's conservation laboratory.

Regarding the chemical's provenances and history, it can be individualized those from the University of Lisbon schools or the museum predecessors' institutions, as the former chemicals from LPS, FCUL and FMUL ⁹; and a second provenance, those from Lisbon district schools – namely the *Passos Manuel* high school ¹⁰ and the former *Veiga Beirão* commercial school.

One of the important issues of surveying this collection, and especially for the history of chemicals industry and its commercial evolution, is the identification of the companies present and its variety. The chemicals with identified manufacturers encompass 38% of the collection, with the remaining 62% being either of unknown producers, local use/reuse, or, by loss of labels and identifying marks, which for this particular evaluation is considered as "lost information". Although, the majority belongs to the German group E. Merck (14,2%), followed by Poulenc-Frères (3%), British Drug Houses (1,4%) and GeHe & Co. A.G. (1%). The identification and quantification of the remaining collection manufacturers can be found in Appendix I.

⁸ Teixeira, C., personal communication, March 2019

⁹ FMUL (1911-present) is the predecessor of the Lisbon Surgical Medical school created in 1836 ^[23].

¹⁰ Created in 1836, following the reform of the Portuguese public instruction that conducted to the emergence of the first district high schools, the *Passos Manuel* high school is still open until our days ^[24].

As the focus of the present study regards the glass containers and their conservation condition, it was important to assess its chemical contents and forms, as a means to determine how and if these substances may be affecting the materiality of the glass. The first results are illustrated in the Figure 1.3. The majority of the collection is thought to contain the original compounds inside, as in some cases the chemicals are still sealed. 49% of the chemicals is composed of solid content, either in powder, crystalline, metallic or mineral compounds, and 22% are composed of aqueous solutions, either clear, coloured, with precipitates or with deliquescent phases. The remaining 29% of the are empty glass containers, with and without labels.

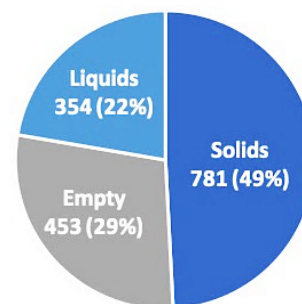


Figure 1.3. Distribution of chemical contents in the collections' glass containers.

From the studies known, few were dedicated to survey chemicals' collections in a broader sense, since normally the largest concerns are expressed over the presence of collections' containing hazardous substances, especially of harmful chemical compounds [8,25]. At the MUHNAC's collection, only 7% (145 chemicals) of the total of the items surveyed were identified as containing toxic and hazardous substances – with the majority of the compounds listed being cyanides (2,4%), mercury (2%), lead (1,7%) or arsenic (0,7%). Similarly, with the survey of the collection's manufacturers, and due to loss of labels ("lost information"), the unidentified chemicals could represent a hazard risk. Although, the museum has an internal policy for the preservation of historical chemicals, including selection criteria and safety disposal of hazardous materials. The identified hazard substances in the collection can also be found in Appendix I.

1.3. Glass composition and manufacture in the 19th century

According to Shelby, glass can be defined as an amorphous solid that does not present long-distance atomic order and with a time-dependent glass transition region. This definition is applicable to all types of glass, of modern and ancient production, despite different chemical compositions. Most glasses found in cultural heritage or in utilitarian purposes are oxide-based glasses, with the most common network forming, or vitrifying, agent being silica (SiO₂) [26].

Since pure silica glasses present high fusion temperatures (around 2000°C), network modifiers or fluxes, are added to lower fusion temperatures. These are usually alkaline oxides, such as sodium or potassium oxide (Na₂O or K₂O), that alter the structure and properties of the glass. The addition of these monovalent alkaline oxides into the silica network leads to the formation of two non-bridging oxygen's, whose negative charge is balanced with the positive charge from the alkaline ion [26-27]. However, the addition of these alkaline fluxes creates a weaker silica structure, therefore reducing its chemical durability, namely the ability of the glass to resist to corrosion and alteration processes [24]. To counter this effect, network stabilizers are added into glass batch. These are generally alkali-earth elements, such as calcium, magnesium or barium oxide (CaO, MgO or BaO, respectively), which, due to their bivalent charge, connect with two non-bridging oxygens in the glass structure, stabilizing the network [27].

The glass industry suffered a quick growth in the 19th century, as a result of the development of the chemical industry and with the discovery and implementation of new chemical processes. The conventional raw materials used until this time in the manufacturing of glass, were replaced by purified reagents obtained through chemical synthesis. These new glasses presented purer and consistent compositions, and industrial production at larger and industrial scale emerged through industrial plants. Therefore, glass manufacturing was able to provide cheaper and larger scale production of glasses for a variety of daily uses that require glassware [28]. To quote Velde "(...)

the age of glass was re-gained in this period in a comparable and more generalized manner than the golden age of glassware in Roman times” [29].

1.4. The aqueous and atmospheric corrosion of glass: a brief overview

Glass is typically regarded as a chemically inert material to most liquids and gases at normal atmospheric and temperature conditions. This condition accounts for its application in industry, research and on a day-to-day basis [30]. Nonetheless, the processes of glass deterioration through the action of water or humidity are a well-known phenomenon, and since the 18th century, where Lavoisier first established that water is the primary agent of glass deterioration [31]. It is throughout the 20th century that the majority of the studies concerning glass deterioration and its corrosion mechanisms and kinetics are developed and their main discoveries are still relevant presently [32]. Glass corrosion studies are a continuously evolving field, with multiple proposed theories on corrosion mechanisms, with the search for a universally applicable mechanism. For the aim of this dissertation, the ionic exchange mechanism is below described.

As glass reacts with water, in form of liquid, vapour or with aqueous solutions, especially with acidic or alkaline, chemical alterations begin to take place at the glass surface. The process will eventually migrate to the glass bulk if it is not halted [32].

According to literature, there are many factors influencing glass corrosion. Although, two are worth to be highlighted: the glass composition and the attacking solution. One of the most fundamental aspects of the attacking solutions, that largely influence the aggressiveness of the attack on glass, is its pH. Glass is sensitive to pH changes, with alterations beginning at high acidic solutions, and becoming increasingly more susceptible at alkaline pH ranges. This will eventually lead to the total dissolution of the glass network as the silica bonds break down [31,33].

Regarding the first factor, glass composition determines the stability of the glass when in contact with the attacking solutions, since the presence of the network modifier cations in the silica network, results in different durability behaviors. Alkali ions are the most easily leached from the glass structure, since they are the least, strong coordinated to the silica network due to its monovalent charge. Alkaline ions with a larger radius will also have the least strong coordination to the matrix, and therefore, will be more easily extracted from the bulk glass to the surface. This is the case of potash-rich glass, as the potassium (K^+) ion presents a larger radius, thus making soda-rich glasses more chemically resistant [33-34].

It is through the introduction of alkaline-earth ions in the glass matrix that its chemical resistance is highly improved. These ions will coordinate with the non-bridging oxygens and halt the alkali ion migration to the surface. When glasses present a low content of stabilizing alkali-earth ions, this decreases its resistance to corrosion. Despite this, if a glass is sufficiently deteriorated, alkali-earth ions can also be leached from the glass matrix towards the surface, weakening the silica network [33,35].

In the presence of water in either liquid, vapour or in aqueous solutions, glass deterioration occurs in two phases [32] as depicted in Figure 1.4.

During the first phase, which happens at $pH < 9$, the first reaction to occur is the ionic exchange, where alkaline ions are leached from the glass matrix to the surface (Figure 1.4., eq.1). In glasses with unstable compositions, cracks will begin to form on the glass surface, allowing for the attacking solution to penetrate into glass bulk and continue the alkali leaching corrosion process, as water enters into the glass structure (Figure 1.4., eq.2). A third step in this phase is the breakage of the silica bonds through the action of the water (Figure 1.4., eq.3). This process of ionic exchange between the solution and glass surface, will result in a superficial layer, rich in

silica species and also hydrated. Water, due to ionic exchange, will be overloaded in H⁺ ions increasing this way its alkalinity and its potential to attack glass [30,32-33].

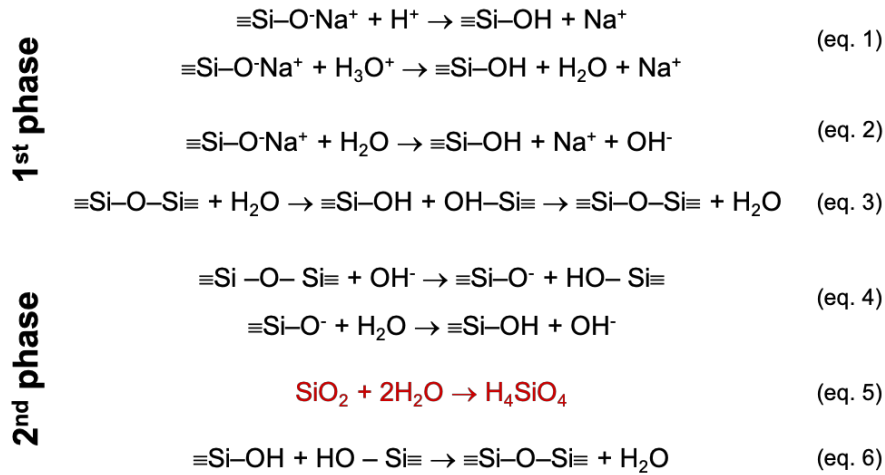


Figure 1.4. Equations for the two phases of the ionic exchange corrosion mechanism, based in [27,30, 33].

The second phase of glass corrosion is after this hydrated layer reaches a pH of 9 [30,32]. At this pH value, the silica network dissolution breaks down the siloxane bonds existent on the glass-solution interface (Figure 1.4., eq.4). In the presence of the formation of new hydroxyl groups, monomeric silicic acid is also formed, which becomes ionized in the presence of these chemical species (Figure 1.4., eq. 5) [30]. This dissolution process is followed by the formation of a gel-layer composed of hydrated silica compounds, which condensate to an amorphous, hydrated and porous layered material, due to network re-arrangement (Figure 1.4., eq.6) [32].

Atmospheric corrosion follows the same mechanisms presented above, in the presence of high humidity, which can be even more aggressive than constant aqueous contact with the solution, as fluctuations of hydration and desiccation forms are constantly altering the surface of glasses [36].

However, the presence of particulate matter, and with high importance the presence of Volatile Organic Compounds (VOCs), can accelerate the corrosion process of glass, especially when combined with the high humidity atmospheres [37-38]. VOCs can be emitted from wooden materials, such as storage and display cabinets, through off gassing, which are known for unleashing formaldehyde, formic and acetic acids. Formaldehyde, specifically or particularly, can oxidize into formic acid [39], which is the second most aggressive agent towards glass corrosion, accelerating the alkali leaching [37].

2. Study of the MUHNAC's collection: methodology

This chapter aims to provide the methodology for the study of the MUHNAC's collection of historical chemicals, developed in two different perspectives. The first section of this chapter concerns the methodology used to conduct the conservation assessment, whilst the second section focuses on the analytical study of two case studies within the collection's glass containers.

The collection survey, as presented in the section 1.2. of the Introduction chapter, provided general insights mainly regarding its dimension, provenance, location and organization of the collection in the museum. This was the first step developed for the beginning of this study. However, a deeper assessment of the collection proved to be necessary, in order to observe its condition and evaluate the internal and external factors which could be influencing the collections' materiality and its stability, with the main focus being on the glass conservation.

2.1. Collection conservation assessment

A conservation assessment consists in a full examination of the environmental and organization conditions in storage and collections exhibitions, allowing the identification of risks and thus prioritizing actions for the improvement of the current conditions^[40]. For the MUHNAC's collection of historical chemicals, the conservation assessment included three steps:

- 1) Identification of corrosion patterns on glass containers – this was achieved through macroscopic and microscopic visualisation, with the aim of establishing groups of corrosion patterns according glass conservation literature;
- 2) Evaluation of the collection locations and environmental conditions – three locations were selected for this assessment, where the majority of the collection was distributed and more representative, namely: at the Chemistry Visible Storage, *Laboratorio Chimico* permanent exhibit and the Technical Storage, presented in Figure 2.1.

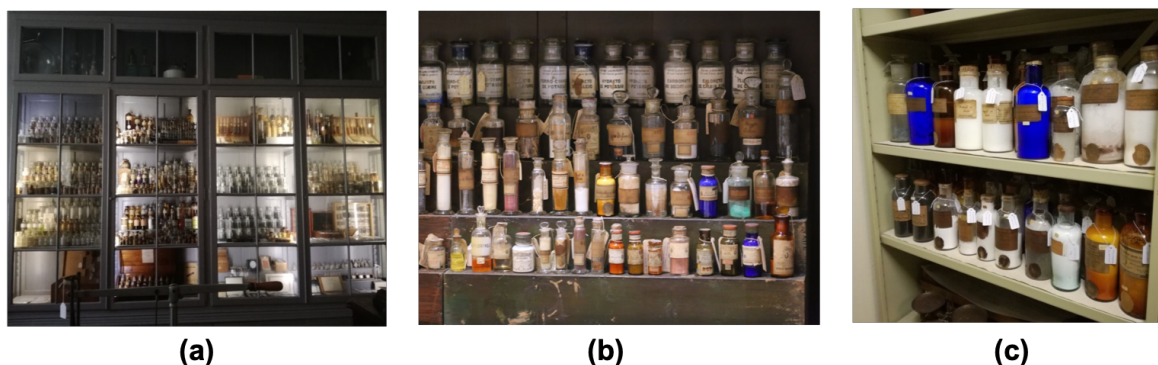


Figure 2.1. Collection locations selected for evaluation and environmental monitoring. (a) The MUHNAC'S Chemistry Visible Storage with the chemicals' cabinet (© Ana Rita Lourenço, 2019); (b) Detail of the *Laboratorio Chimico* permanent exhibition chemicals cabinet (© César Garcia, 2019); (c) Detail of the Technical Storage chemicals cabinet (© Ana Rita Lourenço, 2019).

Besides the assessment of general storage and housing conditions, the following factors were also individually measured or permanently monitored with dedicated equipment, since they may influence directly the collections' preservation:

- Temperature and relative humidity monitored inside the chemicals' cabinets and shelves. The aim was to assess the possibility of the existence of a micro-climate which can favour glass deterioration or a further advancement of its corrosion mechanisms, as the cabinets are generally closed, either in display or in the Technical Storage. For the Chemistry Visible Storage, the measurements occurred between December 2018 to August 2019. The remaining locations were measured from February to August 2019.

- Light measurements, especially concerning chemicals and labels' photostability and photo-sensibility;
 - Formaldehyde concentration in the wooden cabinets, with the intent of assessing possible oxidization into formic acid, as described in literature ^[37,39], which in turn could be affecting the glass containers and promoting corrosion mechanisms.
- 3) Conservation condition of the glasses and risk assessment – through an evaluation and classification of the conservation condition of the glass containers in the MUHNAC's collection, developing a specific conservation condition scale. Additionally, a risk assessment analysis was also performed, taking in consideration the most relevant deterioration agents to this specific collection and applying them to the glass, but also extending this evaluation to the labels and chemicals, to achieve a global assessment of the entire collection and its composing materials. These steps were of major importance to the study, as they allowed for the quantification of the conservation condition rates observed in the glass containers, as well as the most relevant deterioration agents in the entirety of the collection.

2.2. Analytical study

The analytical study of the MUHNAC's collection was achieved through the selection of two separate case studies. For the first technique, employed, glass containers which presented a superficial humid and smeary surface were selected for a superficial pH measurement. This was achieved by using a flat-headed pH electrode with a water medium, as described by Tse ^[41]. The method scheme is shown in Figure 2.2.

Due to the collection dimension, and in order to perform an analytical study to determine possible causes for the observed corrosion patterns in the glass containers, a case-study was selected with coherent glass morphologies that presented significant glass alterations.

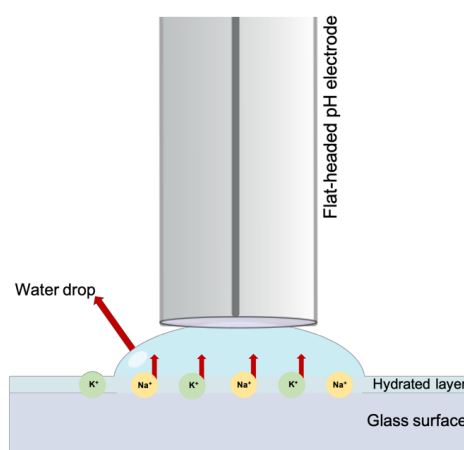


Figure 2.2. Methodology for the pH measurements of glass surfaces (© Ana Rita Lourenço).

A portable set for chemical analysis containing 74 glass containers, was selected for the main analytical study. Information on the selected case-study can be found in Appendix II.

The following techniques were employed in this case-study:

- 1) Portable X-Ray Fluorescence (p-XRF), to determine the chemical composition of the glasses. This analysis was performed *in situ* and with automatic quantifications of the elements identified. A further data analysis was employed, since p-XRF is reported to have a high error associated due to surface conditions ^[42].
- 2) Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES) and High-Performance Ionic Chromatography (HPIC), for the determination of both elemental concentration and ionic species present in each of selected samples of aqueous chemicals. The combination of these two techniques was crucial for the confirmation that the collected samples matched the labels on the containers, and also, to determine if there were any glass products dissolved into the solution, as a result of glass corrosion mechanisms.

Equipment descriptions and analytical conditions can be found in Appendix III.

3. Study of the MUHNAC'S collection: results and discussion

In this chapter the results and discussion regarding the work developed within the study of MUHNAC's collection of historical chemicals are presented, following the methodology developed in the previous section. It comprises the conservation assessment (Section 3.1.), the analytical study of the glass containers (Section 3.2.) and concludes with a proposal of procedures for the MUHNAC's collection (Section 3.3.).

3.1. Conservation assessment of the collection

For this section, the focus of the conservation assessment is exclusive to the glass containers of the collection, due to the presence of corrosion patterns.

3.1.1. Identification of glass corrosion patterns

The portion of the collection that includes glass containers – 1589 items – was evaluated for the presence of glass corrosion patterns. In this part of the assessment, 8 groups of pathologies associated with glass corrosion were observed, accounting to a total of 550 entries. These corrosion patterns are consistent with specific literature and can be associated to the mechanisms described in section 1.4. of the Introduction chapter. They occur due to chemical processes that alter the morphology and structure of the glass, which in turn, result in a visual alteration patterns.

In the MUHNAC's collection, these patterns were macroscopically observed in the majority of the cases. In the 550 entries identified and associated to each corrosion pattern, a single glass container may include additionally one or more corrosion patterns of similar magnitudes. The purpose of the present section is to present the total quantification of corrosion patterns found and provide a brief description of each of the employed terms, in accordance to what is observed within the collection and referenced literature.

The identified corrosion patterns and the number of occurrences per group are represented by decreasing order in Figure 3.1.

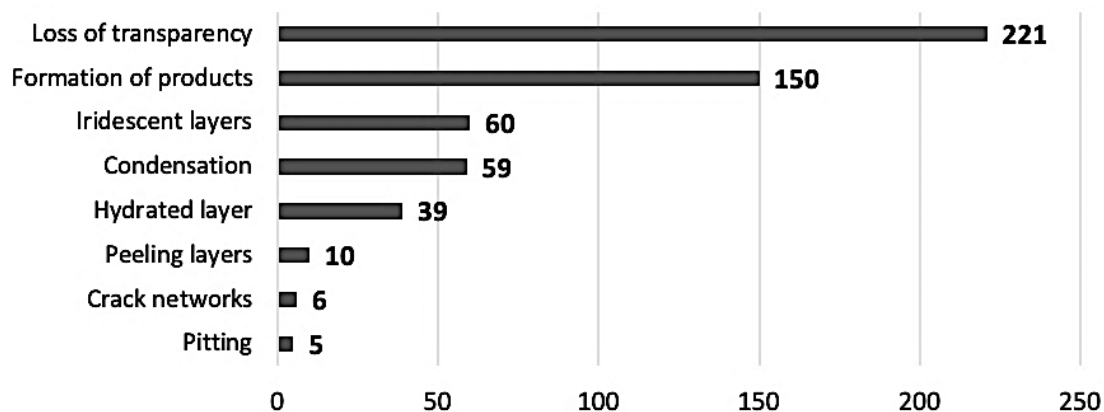


Figure 3.1. Graph representing the quantification of the number of entries per group of corrosion patterns found in the glasses of the MUHNAC's collection of historical chemicals.

The first two identified groups in Figure 3.1. are the loss of transparency and formation of products. These are broad terms that can be further divided into specific patterns of alteration. The remaining corrosion patterns identified a single type of glass alteration.

The majority of the registered patterns are in close association with the corrosion mechanisms explored and its progressive advancement, as was previously explained. These will in turn lead to superficial alterations, influencing transparency due to the altered glass layers, as well as any formation of superficial alteration products.

It was also noted that corrosion patterns are more prevalently on the inside of the glass containers and also, in glasses that don't appear to come from commercial manufacturers. The previous conditions of the collection can be a factor to consider in regard to the variety of corrosion patterns observed, as the former environmental and storage conditions, particularly before the musealization of the collection, are in its majority unknown or undocumented. This is perceptible – chemicals were use or kept until they were considered not relevant anymore as scientific resource for teaching and research. Thus, they could have been exposed to several and unknown environments and actions.

A similar study to the one being taken with the MUHNAC's collection was found, in which it was carried out at the Swiss National Museum, in Zurich. This study included the observation of 342 historical pharmaceutical containers –, presented the same conclusions in their collection. The insides of the containers show more advanced glass corrosion patterns, such as smeary and iridescent surfaces, as well as cracked structures, than on the outsides. The authors also highlighted that these damages can be associated both to their display – in open, wooden shelves –, and due to the variability of the environmental conditions. These factors result in a manifestation of a micro-climate on the inside of their containers [43].

Table 3.1. Presents all the identified groups and sub-manifestations within each group with macroscopic and microscopic photographic reference, with more specific numbers associated to each corrosion pattern.

Table 3.1. Identified corrosion patterns in glass containers, obtained through macroscopic and microscopic observation. Number of entries per damage are expressed between parentheses.

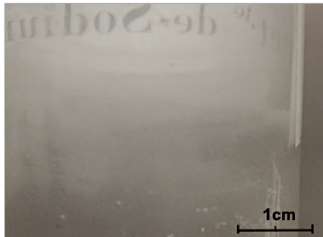
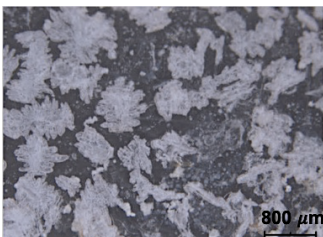
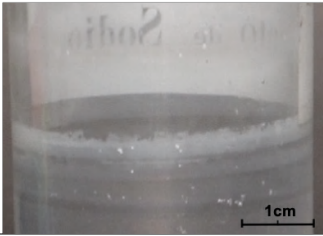
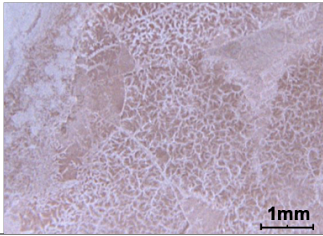
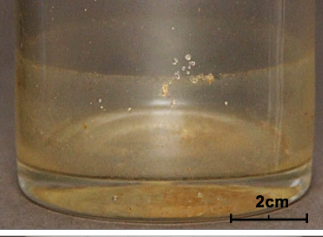
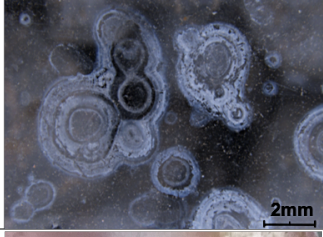
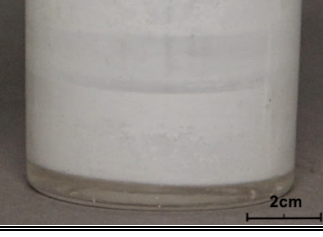
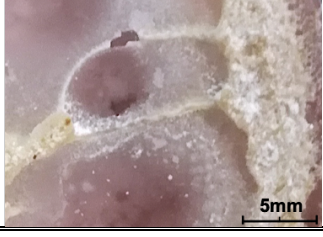
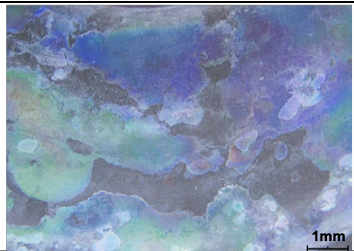
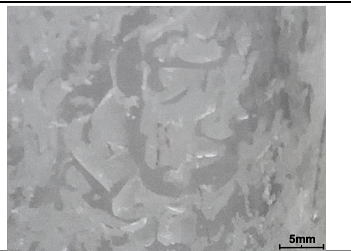

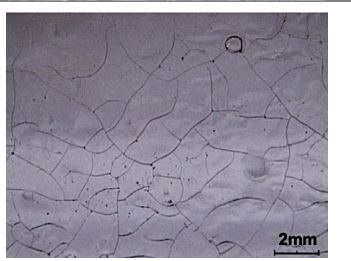
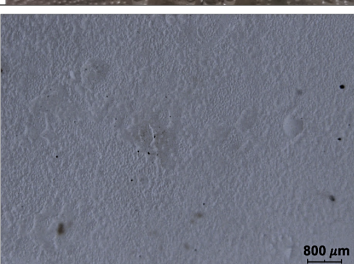
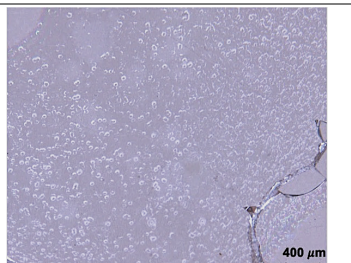
Loss of transparency (221)	Dulling (70)		Formation of products (150)	Deposits (97)	
	Halo-effects (36)			Dendritic crystals (19)	
	Staining (71)			Ring patterns (15)	
	Severe opacification (44)			Crusts (19)	

Table 3.1. (cont.) Identified corrosion patterns in glass containers, obtained through macroscopic and microscopic observation. Number of entries per damage are expressed between parentheses.

Iridescent layers (60)		Peeling layers (10)	
Condensation (59)		Crack networks (6)	
Hydrated layer (39)		Pitting (5)	

According to literature, loss of transparency can be characterized as the glass surface starts to lose its clearness and becomes either translucent or completely opaque ^[31]. Within the MUHNAC's collection it is possible the identification of the following:

- Dulling is defined as the glass loses its transparency and appears with a slight haze or cloudy effect ^[31]. This is the most frequent pattern associated to the loss of transparency
- Halo effects, referring to glasses that present several halo-like structures around the diameter of the container, which may appear as a mark where the chemical may have been in contact with the glass for a significant period of time. This pattern is most commonly found in containers with liquid substances; nevertheless, some solid substances in the collection also exhibit this pattern.
- Staining, may derive from the action of the chemical itself, leaving a superficial colour alteration which may result in some cases, in the inability to see the contents on the inside of the glass. This stain may also contain traces of the previous chemicals, which is unknown if it may continue to affect the glass.
- Severe opacification is defined by glasses that present a milky or total white opacified surface. These may be related to the overlapping of alteration layers, due to the corrosion processes over the original glass surface ^[31]. In the collection, this effect can be manifested both on the inside and on the outside of the container.

The formation of products on the glass surfaces is diverse and it can derive from multiple origins. Frequently these can be found under the form of:

- Deposits on the surface of the glass, usually under the appearance of small crystals or salts ^[31,34]. Most deposits appear on the inside of the containers and it is difficult to determine whether they may be a corrosion product, resulting from the interaction of the glass with the

micro-climate inside the containers. Or if they are in any way related to the chemical. However, it is noticeable that they are found aggregated to glass surfaces and appear to be drawing moisture. Hygroscopic particles present further damage, as they can promote an environment for the development of corrosion mechanisms.

- Dendritic crystals, appear as networks of connecting crystals, forming dendrites. These are harder to detect and usually require the use of raking or transmitted light.
- Ring-patterns are commonly found in solid chemical samples, especially of metallic substances. They create concentric patterns that appear to have lamellar structures. According to Bianco *et al.* study, this is pointed as being caused by the oxidation of metals in contact with the glass surface, especially of antimony or titanium origins ^[44].
- Crusts are the formation of a thick and external layer, that solidifies on top of the glass ^[31].

Iridescent layers are one of the most familiar patterns in glass corrosion. They appear due to overlapping of thick, silica-rich alteration layers after the alkali leaching has occurred. This results in the diffraction of the light rays, creating an iridescent appearance ^[45]. At MUHNAC's collection, these usually appear as an overall, lightly iridescent layer or through localized layers. In any case, neither are severe.

Condensation is the presence of small water droplets on the glass surface. This create a constantly wet surface in which corrosion mechanisms may take place. Continuous cycles of drying and re-condensation, mirrors the effect of atmospheric corrosion in high humidity environments ^[31]. A glass container with a solution prone to condensation may be due to a volatile liquid or due to inappropriate environment conditions that promote solution evaporation and condensation.

The presence of an overall hydrated layer can denote that a water (or aqueous solution) film has been formed. These surfaces have a sticky and smeary appearance, and they may be associated with the formation of a silica gel layer, and, thus, in active corrosion ^[31].

Peeling layers, indicate that the glass has become structurally altered and with flaking layers that present weak adhesion to the glass bulk. As the glass continues to flake, the process of corrosion develops further into the glass bulk ^[31].

Crack networks represent a fragile glass structure weakened through networks of cracks, which may result in the irreversible collapse of the glass structure, unless specific conditions are created for these glasses. The phenomenon observed specifically in the MUHNAC's collection appears either as spontaneous cracking of the glass surface, which, as described by Davinson, may result from constant hydration and dehydration of the surface, resulting in structural strain from the loss of water volume ^[31]. It can also be associated with advanced stages of crizzling, as deeper cracks form within the glass surface. It may start to cover the entire of the glass surface and become more prevalent in areas that have been exposed to moisture – such as the case of the inside of the containers, due to the existence of a micro-climate ^[46].

Pitting is the localized loss of material in the form of pits and can disseminate into crack networks as corrosion advances. According to literature, the formation and growth of pits can be linked to a continuous loss in matter from the glass bulk ^[47]. At MUHNAC's collections this effect was only possible to observe through microscopic equipment or with the use of raking, or obliquely beamed light.

To conclude, although the focus was the observation of corrosion patterns as a result of chemically induced damage, physical damages were also accounted in the collection. These are

found under the form of fissures (21 entries), fractured glasses (6 entries), and lacunae or missing glass pieces (10 entries). These damages could have occurred due to the fragility of the glass that may be significantly altered, and thus caused by its inherent characteristics or through influence of external factors, such as inappropriate handling, or, due to unknown actions in the course of the objects' history and former use.

3.1.2. Collection locations and environmental conditions

As described in the methodology (Chapter 2), three locations were chosen for the environmental assessment: 1) the Chemistry Visible Storage; 2) *Laboratorio Chimico* permanent exhibition; and 3) Technical Storage. Before presenting and discussing the obtained results, a brief description of each location is provided:

- 1) The Chemistry Visible Storage has a double purpose of being a storage and a display room where the majority of the MUHNAC's chemistry collection is preserved ^[21]. It is located at the ground level of the museum main building, in a room with large windows, protected with UV filters and micro-perforated blinders, minimizing the amount of external natural light. The room lightning system is in part constituted of fluorescent lights, and the majority of LED typology, particularly in the wooden chemicals' cabinet. This location is abundantly surrounded by wooden materials as there are remaining cabinets where the rest of the original objects are stored; the floor is covered in a wood-derived floating floor. The collection at the Chemistry Visible Storage is strongly heterogeneous, presenting artefacts with wood, glass, metal, rubber, plastic and paper materials, and some composites
- 2) The Laboratorio Chimico is located next to the Chemistry Visible Storage. This is a space where the natural light is limited, filtered from a skylight on the top of the laboratory ceiling. The exhibition is present in the historic chemistry laboratory, composed of former wooden benches with ceramic tile surfaces. The collection is composed mainly by glass, ceramics and metals, all stored in the original cabinets at display in the laboratory space. One of the cabinets is full dedicated to the exhibition of the historic chemicals. The chemicals' cabinet presents internal illumination, in the form of incandescent filaments, where the majority have already failed.
- 3) The Technical Storage, built in the 1990's, and whose location in the building is here undisclosed due to security reasons, is composed by metallic compact rolling cabinets with shelves, dedicated to the storage of scientific instruments, where the chemicals are kept according to its provenance in 4 racks. The storage cabinets are permanently closed as well as the Storage itself, unless access is needed. The walls are in concrete and the floor is made of ceramic material. The exterior windows of the Storage are always closed with shutters and no natural light comes inside. Regarding the artificial light, it is mainly switched off and the ones located directly over the cabinets are still of fluorescent typology, although the remaining lightning system is already of LED typology. The Storage harbours heterogeneous collections and materials – deriving from small to large instruments, but also to laboratory equipment and utensils, paintings, portraits, and furniture.

A summary of the environmental parameters measured in each of the collection locations is provided in the Table 3.2. For full data compiled regarding temperature and relative humidity, radiation and formaldehyde measurements conducted, refer to Appendix IV. For the interpretation of the data presented in the table below, in the case of temperature and relative humidity measurements, two parameters are presented – the interval of average values for the measured periods; and the average variation of minimum and maximum registered values for a certain parameter in the same time frame. Illuminance and Radiation data are presented according the reference measurement units, as well as in the case of formaldehyde concentrations. All data

compiled was compared to literature's reference values, from conservation literature and health and safety regulations.

Table 3.2. Summary of the obtained data for the measured parameters at the different collection locations, over the period of December 2018 to August 2019, in comparison with the Classical Meteorological Station of the *Instituto Dom Luiz* (IDL) and with literature reference values.

Measured parameters	Collection locations				Reference values	
	Chemistry Visible Storage	Laboratorio Chimico	Technical Storage	Meteorological station ¹¹		
T (°C)	Average	16 - 26,3	16,4 - 23,9	16 - 26	11,4 - 22,7	- General: 18-22 [48, 49]
	Average variation	4,2	2,9	4,6	17	- Fluctuations <2-5
RH (%)	Average	50 - 59,3	53,5 - 62,9	47,7 - 56	63,1 - 84,7	- General: 50-60 [46, 48-49]
	Average variation	13,7	27,3	26,8	66,5	- Glass: 45-50 Fluctuations <5-10
Illuminance Radiation	Lux	20,7 - 72,6	16,2	50 - 143,3		50-80 lux [50-51]
	μW/lm	1 - 9	4	5 - 9		30-75 μW/lm
Formaldehyde concentration (ppm)		0,01	0,01	---	----	- Collections: 0,01-0,02 [39, 52] - Health ¹² : 0,075-0,08

Starting with the Chemistry Visible Storage conditions, the range of average temperatures for the measured period follows a gradual 10°C increase, over the course of the 9 months, with an average variation of 4,2°C between the maximum and minimum registered temperatures. The months with the largest variations registered were January and May. The lowest registered temperature was in January (14,3°C), and the highest was in August (28,2°C). As for the relative humidity parameter, these present fluctuations throughout the months with a high average variation (13,7%), especially when compared to reference values. The highest recorded variations occurred in March and June, and the lowest registered value was in March (43,9%), whereas the highest was in January (65,1%). As for the light conditions inside the chemicals' cabinet, both measurements were according the reference values, when comparing with literature for light sensitive materials, such as paper artefacts ^[50, 53]—, a concern that was expressed either for the labels and for chemicals, as they may deteriorate with light ^[54]. Formaldehyde concentrations are also within reference values.

Evaluation the conditions at the *Laboratorio Chimico*, it could be observed in this location that temperature values presented a lower increase in temperature over the course of the measured period (7,5°C), and it increased steadily over the months. Temperature variations are also lower, with an average of 2,9°C, in which the months with the largest variations are March and May. The lowest registered temperature was in February (15,3°C), whereas the highest was in July (24,9°C). With regards to the relative humidity, this is the location from those evaluated with the most fluctuations, presenting an average variation of minimum and maximum values of 27,3%, exceeding the reference values in over 15%. The months presenting the highest relative humidity

¹¹ Data obtained from the Classical Meteorological Station of the *Instituto Dom Luiz* (IDL), Faculty of Sciences of the University of Lisbon (FCUL): <http://dados-met-idl.campus.ciencias.ulisboa.pt/>

¹² Health is an important parameter when dealing with compounds such as formaldehyde, as they not only affect collections, they also affect the human health. Formaldehyde is a carcinogen, which is defined as “an agent (whether chemical, physical or biological capable of increasing the incidence of malignant neoplasms)” ^[10, 52].

fluctuations were between February and May. The lowest registered value was in June (36%), whilst the highest was in July (62,9%). As well as in the Chemistry Visible Storage, both light measurements and formaldehyde concentration are considered within the referenced values.

The Technical Storage presented the same gradual increase of temperature over the period of 7 months, with a 10°C increase. It is, however, the location with the largest variation in temperature over the time frame – 4,6°C variation –, with the highest temperature variations registered in February and May. The lowest temperatures were verified in February (14,3°C), and the highest was in August (27,7°C). Regarding the relative humidity, it also presents high average fluctuations, with an average of 26,8%, well above reference values, in similarity with the *Laboratorio Chimico*. The largest difference is that the storage shelves are not enclosed in the same way as the cabinets are in the remaining locations, and so, these are concerning values for the entire storage room. The lowest registered value was both in March and June (35%), while the highest was in May (70,4%). In comparison in the previous locations, light measurements present higher values, with values not in conformity with the reference values – over the 50-80 lux range. However, as this Storage is less accessed than any other due to its restrictions, compact cabinets are always closed and artificial light sources are not constant or directly pointing to the chemicals' collection, these are negligible values. Formaldehyde concentrations were not performed in this location, as the collection is stored in metal shelves.

When comparing the values of the three locations with the data obtained from the IDL meteorological station, which is located at the museum complex, it is possible to note that the temperatures match the variation from the data registered on the exterior. The coldest temperatures in all the locations were January and February, and the warmest were in August. This trend is also observed with the relative humidity values, through the months' variations, as in all of the measured locations, when large fluctuations occur outside the museum building, they are also reflected at the interior. This means that the museum building, besides of being part adapted in the 20th century for a museum function, and another part with pre-existent structures from the 19th century (Chemistry Visible Storage and the *Laboratorio Chimico*), is highly susceptible to external climate variations, that directly reflects in the storages and exhibitions indoor conditions as those evaluated

In conclusion, all locations evaluated are in need of environmental improvements or control, with special regards to the high registered humidity fluctuations, particularly at the *Laboratorio Chimico* and the Technical Storage. Although, all the locations evaluated includes heterogeneous collections of instruments with diversified materials as mentioned, the high humidity fluctuation could create a specific impact in glass structure materials, since humidity is responsible for the development of corrosion mechanisms in glass. As Koob *et al.* note, particularly for glasses that are already in corrosion processes, the fluctuations need to be lower than 2%, and preferably at an atmosphere between 40-42% relative humidity ^[55]. In the case of the MUHNAC's collection of historical chemicals this could be a challenge to achieve by the aforementioned. It is also to be highlighted that despite of low formaldehyde concentrations, formic acid may still be present in the atmosphere and thus, should be accessed in the future as it is of concern to glass collections ^[37].

3.1.3. Glass containers' conservation condition and collections' risk assessment

Following the previous identification of the corrosion patterns at the MUHNAC's collection, and the evaluation of the collection's environment, the final part in the conservation assessment section is the development of a conservation condition scale that can relate the observed and identified damages to a rating system. This scale is based on terminologies and descriptions adopted by Ashley-Smith ^[56] and Keene ^[57], and adapted from the museums' general conservation

scale, which is also based on the Portuguese Institute for Conservation and Museums (ICM) ^[50]. The developed condition scale is presented in Table 3.3. and provides a description for each of the grading criteria, as well as which corrosion patterns are associated to each grade and its quantification on the MUHNAC's collection.

Table 3.3. Conservation condition scale applied to the glass containers of the MUHNAC's historical collection of chemicals. The quantification for each grading criteria is also provided.

Grade	Description	Quantification in the MUHNAC's collection
Good	The glass container is stable, with no apparent active conservation problems. It may contain some degree of superficial or physical alterations. These are the glasses that encompass <u>physically induced damages</u> , such as fissures, lacunae or missing glass pieces. <u>Dulled glasses</u> also fits in this criterion.	69,5%
Fair	The glass container may present partial structural damages, such as <u>fractures</u> , or active corrosion at small or controlled scale. Glasses that fall into this parameter should be monitored regularly to assess the advancement of the corrosion. These are the glasses that encompass <u>halo-effects</u> and <u>stains, deposits, dendritic crystals, ring patterns, iridescent layers</u> and <u>condensation</u> .	22,8%
Poor	The glass container is structurally and chemically unstable, with active corrosion mechanisms. These are the glasses that encompass the following corrosion patterns: <u>Severe opacification, crusts, hydrated layers</u> and <u>pitting</u> .	6,7%
Unacceptable	The glass container presents extensive structural damage, with very unstable materials and loss of material. These are the glasses that present <u>crack networks</u> and <u>peeling layers</u> .	1%

The table comprises both the previously identified corrosion patterns, as well as the physical damages found in the collection, which amount to 587 entries. When distributing the associated damages to the conservation condition grades, it is possible to note that 69,5% of the collection is in a good condition. This encompasses slightly damaged glasses, that ultimately are not in immediate risk of loss and glasses that present no damages. As for the remaining described grades, 22,8% of the collection is in a fair condition, 6,7% in poor, and just 1% in an unacceptable condition. This overall reflects that, despite all the identified corrosion patterns, the large majority of the collection is in a good conservation condition. Nonetheless, the identified patterns, that were graded from fair to unacceptable conditions, need regular monitoring, and in some cases, the implementation of preventive and curative measures.

Furthermore, a risk assessment to the collection was also performed to its entirety. According to Waller ^[58], risks are “*the change of undesirable change occurring*”. Risk assessment, according to the author, should look at the risks that can be identified in a collection, and rate the impact that such a risk could have on an object or collection ^[58].

The purpose of this work was not to perform a full risk assessment with risk magnitude calculations, but rather to assess which deterioration agents could have a larger impact of damage to the collection, in a condenser table and for future reference. The risk assessment for the MUHNAC's collection was applied to the three materials that compose the object itself – the labels, the glass container and the chemical substances. The purpose was to evaluate the most

relevant deterioration agents to the collection, following the results from the conservation assessment. The compilation for risk assessment can be found, for example, in Michalski^[59] or in the ICM^[50]. Table 3.4. expresses the risk assessment performed for the MUHNAC's collection.

Table 3.4. Risk assessment of various pondering factors in the MUHNAC's collection of chemicals.

Pondering factors in collections of historical chemicals		Material components		
		Labels	Glass containers	Chemical substances
Susceptibility to type of deterioration	Physical agents	3	4	3
	Chemical agents	4	3	4
Susceptibility to environmental deterioration	Incorrect RH%	4	3	4
	Incorrect T°C	4	2	4
	Light	4	1	4
	Pollutants	3	3	3
Susceptibility to other deterioration agents	Water	4	3	3
	Fire	4	4	4
	Pests	4	1	2
	Dissociation	4	4	1
Safety and hazards		2	3	4
Historical integrity		+++	++	+

Rating system:

- Risk is evaluated from 1 to 4, where is 1 – Lowest risk; 2 – Partial risk; 3 – Concerning risk; 4 – High risk;
- Historic integrity is evaluated in + signs, where the highest number of signs indicated the importance to the historic integrity.

The susceptibility of the different materials to physical and chemical agents is tied with the intrinsic features of the materials. E.g. Glass containers have a higher likelihood of breakage due to the inherent fragility of glass, whereas chemical damage may occur to all materials, with special regards to the labels and chemical substances, as they are the most sensitive to alteration.

Environmental deterioration, as discussed in the present dissertation, can affect all the materials due to chemical alterations. Other deterioration agents, such as water, fire, pests or dissociation, although not of primary concern at MUHNAC, in the event of their appearance, it can have a large impact on the collection. Safety and hazards are a paramount factor due to the nature of the collection itself, and how a chemical substance may contaminate the rest of the composite object, or an entire collection.

Historical integrity, taking after Keene^[57] look into the components needed for the collection to function with regards to its historic value. For example, if a chemical substance is deemed hazardous and it must be disposed of, its container and label may still contribute to heighten the collections representativeness.

3.2. Analytical study of the glass containers

In this section, the results and discussion of the analytical techniques applied to two different samples of the collection are presented. Section 3.2.1. concerns the measurement of the superficial films formed on the external glass surfaces. Sections 3.2.2. and 3.3.3. concerns the

techniques applied to the established case-study of the collection, as previously described on the methodology chapter (Section 2.2.).

3.2.1. pH measurements of the glass surfaces

This test aimed at the detection of any superficial glass alkalinity, as a possible indicator of active glass corrosion mechanisms. The glasses containers considered for this test were those that during the conservation assessment, seemed to present a smeary surface that felt slippery when touched.

For the purposes of this measurement, a deionized water drop used as a medium was placed in contact with the glass surface for the measurements, presenting a pH of 6,70. A total of 5 glass containers' surfaces were measured.

The results from the measurement of the water drop medium in contact with the aforementioned film showed an increase pH, when compared to the water drop medium value, with pH values ranging from 6,89 to 7,93, lowest and highest values registered, respectively.

For further comparison, this test was replicated in glass containers that did not seem to present a superficial film and no significant alterations to the pH level were found. The values show a variation of 0,1 to 0,3 of the pH from the water drop medium.

This shows that in all the measured surfaces that presented a superficial film, there is an increase of pH value, although not drastic. However, this test demonstrates that the glasses appears to be in active alteration at the surface of the glass, resulting in visual and sensorial alterations. Without monitorization or halting the process, the pH is likely to continue increasing, following corrosion mechanism trends and eventually triggering the dissolution of the silica matrix ^[30,32].

3.2.2. Composition of the glass containers

The purpose of determining the composition of the glass containers was to access if it could be an intrinsic factor in the deterioration of the glasses.

Other studies have shown that, while p-XRF has a high associated error to the detection of light elements, it can be used to divide between composition groups, and it is usually accurate with the determination of the heavier elements or trace elements ^[60-62]. The major advantage of this type of analysis is the ability to be used, *in situ*, without the need of objects transport, or the samples removal as anon-invasive technique ^[42].

As the full chemical composition of the glasses cannot be determined accurately through this technique alone, a data analysis approach was taken, following the methods explored by Coutinho *et al.* ^[63]. Through the comparison of elemental peak areas in the obtained spectra and the values obtained through the automatic quantification of the analysed objects. This data analysis approach is further explained in Appendix V.

The results determined that there is a correlation between peak areas and the automatic quantifications made by the equipment's software. Therefore, these quantifications were used to determine the different compositional groups found in the case-study. The defined groups can be found in Figure 3.2, which show a clear distinction between two compositional groups – with the majority of the containers falling into Group 1, followed by Group 2, and a third, considered as an outlier group, with a vastly different composition from all the other containers. Within the two major compositional groups, other outliers can be identified. These present significant differences in the quantification, likely due to the superficial conditions of the measured areas, which may present alteration areas, affecting the final quantification ^[42].

The automatic quantification results obtained for all the 74 measured glass containers can be found in Appendix VI.

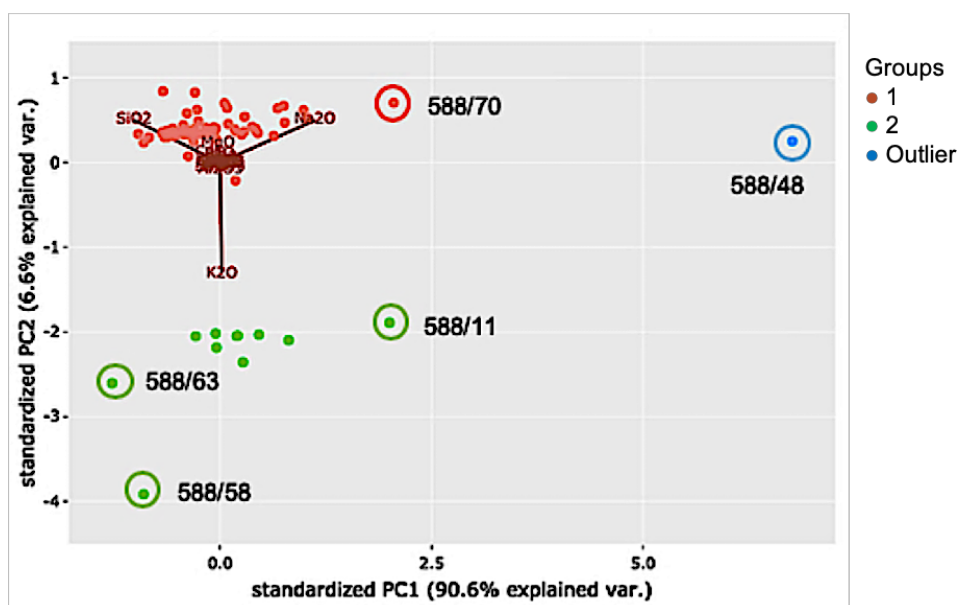


Figure 3.2. PCA scatter plot of the compositions of the 74 measured objects through p-XRF. Outliers for each group are circled and the inventory number is provided.

The average composition of the two main compositional groups is expressed in Table 3.4., presenting the oxides that explain the data variability and the differences found in the compositions between both groups.

Table 3.5. Average values (with standard deviation) of the 2 groups defined by PCA analysis. Oxides shown are based on PCA importance. Relative accuracy (R.A.) is given based on analyses of CMOG A glass standard. Na₂O values are obtained through the sum of all oxides, minus 100. Values in weight percent (wt%).

Groups	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	SO ₃	Cl	K ₂ O	CaO	MnO	PbO	Sb ₂ O ₅
1	12,5 ± 2,6	1,5 ± 0,3	0,0 ± 0,1	76,6 ± 2,2	1,1 ± 0,4	0,1 ± 0,0	0,3 ± 0,2	7,0 ± 0,9	0,2 ± 0,0	0,4 ± 0,2	0,2 ± 0,1
2	12,2 ± 3,7	0,8 ± 0,2	0,3 ± 0,2	74,0 ± 3,7	1,0 ± 0,4	0,2 ± 0,1	4,0 ± 1,1	6,6 ± 0,8	0,1 ± 0,0	0,0 ± 0,1	0,3 ± 0,2
R.A.	10,4	19,9	69,5	4,2	-	-	7,2	2,4	11,1	56,9	24,6

When comparing the results between the two determined groups it is possible to conclude that both groups present the composition of soda-lime-silicate glasses, with the major difference being the higher K₂O contents in group 2. The glasses present a low content of alumina – a compound which is known to increase glass durability -, however the concentration of MgO and CaO could have a stabilizing role on the glass batch. The overall composition of the glasses is close to the industrial standard glass batches, which are known for its stable properties, due to their applications. This is also consistent with the chronology at study, as during the 19th century glasses made for utilitarian purposes used stable raw materials [26, 28].

When looking at the first two groups, one interesting conclusion is that Group 1 is composed of the containers with Portuguese labels, while Group 2 has majorly French labels. This may indicate that the containers come from multiple provenances and are now simply stored inside the same portable set, either as a result of its history of use or as a display settle intentionally made for the Visible Storage musealization.

Despite the correspondence of the identified groups with those that are considered stable, it is still possible to find corrosion patterns in the glasses from both compositional groups. There is no

apparent difference between incidence of corrosion patterns and the compositional groups identified. Group 2 presents the majority of the corroded glasses, but they are also in a lower quantity than those of Group 1. Table 3.5. compiles the corrosion patterns found per group, using the terminology defined in section 3.1.1..

Table 3.6. Corrosion patterns found in the containers of the different composition groups.

Group	Total	Corrosion patterns						
		Condensation	Hydrated layers	Iridescent layers	Loss of transparency	Formation of products	Pitting	Peeling layers
1	62	16	2	1	35	16	1	1
2	11	2	-	-	5	4	-	-

In conclusion, p-XRF proved to be useful in distinguishing between different compositional groups, however, no relation between compositional differences and corrosion patterns could be defined.

3.2.3. Composition of the aqueous chemical solutions

For a further characterization of the chemicals, samples from the inside of the previously analysed containers were collected. The selection criteria and sampling of the analysed solutions is described in the sections a) and b) of Appendix VII. The selected analysed samples served two purposes: first, to identify if the chemicals present inside the containers match their labels; and second, to determine if any glass dissolution products could exist in the solutions, as they are in aqueous form.

Through the use of ICP-AES the elemental concentration of the samples was determined and required no sample preparation, therefore, minimizing contamination from external agents, as one of the requirements of the technique is that the samples must be in liquid form^[64]. It was used to determine the presence and concentration of the elements, as well as to determine if there was any concentration of possible glass component elements – such as Si, Na, K or Ca – that may have been leached into the solution through corrosion mechanisms. One of the disadvantages in ICP-AES is that it only offers an elemental analysis, while the solutions are presumed to be molecules.

Therefore, for the detection of the anions in the selected solutions, these were submitted to HPIC analyses. This technique aims at identification of the presence of ionic species within the sample, for further confirmation that the solutions sampled match the labels, and to specifically confirm the presence of the sulphate, chloride and phosphate anions.

Through the combination of both techniques it was possible to determine that the contents of the 9 sampled match their labels. Furthermore, through HPIC it was possible to determine the presence of chloride in all the samples, including in the chemicals that were not chloride-based compounds, with the exclusion of the magnesium mixture. In the case of the non-chloride-based compounds, chlorides concentration is much lower than either the sulphates or the phosphate. This could likely result from the preparation into aqueous solution, as chloride species are frequently found in water^[65]. The ICP-AES and HPIC concentration results for all the samples collected are presented in section c) of Appendix VII.

Through the analytical confirmation that the chemicals sampled match the labels on the containers, a comparison approach was taken regarding the pH of the solutions to the elemental concentration of possible glass. This evaluation intended to determine if with increasing pH levels

in the analysed chemicals it is possible to find higher concentrations of the aforementioned elements. Table 3.6. compiles the results obtained.

Table 3.7. Values for elemental concentration of Si, Na, K and Ca determined by ICP-AES (in mg/L, or ppm), in comparison with theoretical pH of each chemical and the pH of the solutions from the collected samples.

Samples	pH of the solutions		Elemental concentration			
	Theoretical ¹³	Measured	Si	Na	K	Ca
Sodium sulphate	7,0	1,61	7,97	7702	8370	0,00
Zinc sulphate	4,0-6,0	5,49	43,93	0,00	1445	9,46
Manganese chloride	4,0	5,65	22,89	5,91	1302	2,77
Magnesium sulphate	7,9	6,86	44,70	16,92	819	12,37
Calcium chloride	8,0-10,0	7,00	7,12	2930	1722	56749
Strontium chloride	5,0-7,0	7,80	35,70	96,45	820	1034
Lithium chloride	6,0-8,0	8,00	35,15	42,29	994	2,24
Sodium phosphate	4,5-12,5 ¹⁴	8,84	44,92	6216	504	0,00
Magnesium mixture ¹⁵	?	9,40	0,00	19,50	281	14,71

When assessing the pH of the solutions, these were compared to the modern version of the same chemicals in aqueous solutions. Looking at the results, it is possible to determine that some of the samples either remain in the determined ranges, or they become more acidic or alkaline. This may indicate alteration in the chemical, that may be due to ageing or the possibility of the solution in which it was prepared might have influenced these results.

With the collected solutions it is possible to note that those presenting pH values beyond the neutral range are also those that show higher incidence of corrosion patterns, namely with the loss of transparency or formation of products in the glass.

Looking at the ICP-AES results, with the exception of sodium sulphate and sodium phosphate, which present high Na values due to being sodium-based compounds, all other analysed chemicals present some degree of Na within the solution. Similarly, with the exception of calcium chloride, again as it is a calcium-based compound, most of the samples also contain some level of Ca.

When comparing to leaching studies in soda-lime-silicate glasses, that measure solutions after glass corrosion were performed, it is possible to note a linear increase in the concentration of glass elements that have been dissolved into the solution, as the pH increases ^[32, 66]. Yet, when looking at the analysed samples, the same results do not follow the same linear trend. This could be due to the fact that the solutions used in other studies are of water, as the solutions presented are of actual chemical compounds, therefore, resulting in a more difficult comparison.

¹³ The theoretical values were consulted through modern chemicals' material safety data sheets (MSDS) from major chemical suppliers and companies – Fischer Scientific, Merck, Labchem.

¹⁴ The values for sodium phosphate vary significantly according to its molecular structure, as it can be found in mono-, di-, or tri- phosphate, which largely influences the pH range. The analyses performed couldn't identify the type of phosphate present in the collected sample and no information was present in the label.

¹⁵ Magnesium mixture is thought to be the mineral Dolomite – a calcium magnesium carbonate ($\text{CaMg}(\text{CO}_3)_2$) (Carneiro, A., May 2019, personal communication).

In all the remainder samples, none are silicates or potassium-based compounds, however high concentrations of potassium can be found, while, although lesser, some concentration of silicon is found. p-XRF showed that potassium is present in the glass compositions, so this could be an indicative of lixiviation of potassium ions. Interestingly, the solution that presents a pH value superior to 9, had no Si identified in the solution, as according to the literature, this is the pH value in which silica will begin to dissolve ^[32].

However, due to the difficulty in comparison with other glass corrosion studies and the fact that these solutions' may be over a century old, it could be the case that the solutions are made of unpurified chemicals, and therefore the found concentrations may have impurities in the form of the typical elements found in glass. Nonetheless, as described above, there is visual evidence of glass corrosion. Further analyses with other solutions and chemicals would be necessary to confirm if there are dissolution processes.

3.3. Procedures for improving the MUHNAC's collection condition: a proposal

The following points are suggestions for further improvements of the collection to ensure firstly, its long-term stability:

- Controlling the environmental conditions, namely temperature and relative humidity fluctuations, as all the evaluated locations presented data that surpasses the reference values that could affect the materials in long-term;
- Monitoring the identified glasses which are in advanced corrosion condition – such as those presenting crack networks, peeling layers, severely opacified or with hydrated layers;
- Developing of a specific conservation plan for this collection, that oversees all the different materials that compose the chemicals and their inter-relationships, for maximum preservation of all the materials in the composite objects.

Additional studies that could be developed in the collection, namely:

- An in-depth air quality assessment should be performed to the collection locations, as a strong chemical scent can be felt throughout the year, intensified during the summer period. The vapours released could be of toxic origin, therefore making this an urgent matter; A suggestion for the Technical Storage would be the transfer of the chemicals to safety cabinets, with extraction. At the *Laboratorio Chimico* this is not recommended, as there are difficulties in the placement of chemical extractors. In the Visible Storage, where the scent is the strongest, it is the location that should be prioritized the installation of an extraction and air renovation system.
- A survey and conservation assessment to both chemical substances and labels. It was noticed throughout the duration of this study that these materials are in various condition grades, and a focused study on these materials could result in a further complementation of the results from the present study and add more information to a specific conservation plan.

4. Preservation guidelines for collections of historical chemicals

This chapter presents the final outcome of this research, with the aim of encompassing the theme of collections' preservation. The goal is to present simple preservation guidelines, that may be applied in similar collections of historical chemicals, so that institutions may find key measures to ensure the collections' long-term preservation.

This is also intended to be applicable a variety of institutions – such as university departments or museums, schools, science centres or in other research institutions that may hold collections of chemicals with historical significance.

The elaboration of this section appears as a necessity due to few factors that were noted during the development of the dissertation – the fact that there is limited literature dedicated either to the collections of chemicals specifically, and even sparsely to their conservation. Nevertheless, the publications made by French ^[67] and Kondratas ^[68] must be highlighted, while applied to pharmaceutical and medical collections, they provide valuable insights and some general guidelines that are reflected within this section. Guidelines and procedures, from a conservation perspective, as well as for practical measures, can be found in Hicks ^[69] and Storch ^[70].

Another driving factor is the accounts of requests for assistance, namely from small institutions for the preservation of their own collections. This is an example that frequently happens to MUHNAC, since the museum already provides regularly conservation support to institutions with scientific heritage – namely in the selection criteria for the preservation of historical chemicals ¹⁶ –, deriving from its consolidated practices regarding the preservation process of its own historical chemicals over the years¹⁷.

For this section, the methodology employed consisted:

- Literature research;
- Gathering knowledge from other collections, namely through a survey sent to selected institutions. This selection was based on the institutions enlisted on the ICOM-UMAC's database ¹⁸. Other replies also were obtained through personal communication with collections' caretakers. The survey aimed to assess collection typologies and dimensions, exhibition and storage conditions, glass container corrosion patterns, safety and conservation measurements, as well as optional questions regarding the deterioration of chemicals or labels. The summary and statistical results from this survey are presented in Appendix VIII.
- Data obtained from the study of the MUHNAC's collection, as a case study for this dissertation.

Before presenting the proposal guidelines for these collections, Table 4.1. presents the evaluation of inherent characteristics and acquired characteristic that each material may present in chemicals as composite objects. This classification is done according Hawks & Makos classifications ^[9]. Although the referenced paper is presented in the context of hazards in collections, this classification can be applied to different material alterations. The authors consider inherent as a characteristic that is associated with the material, since its genesis, whilst acquired characteristics are those that may have been intentionally or unintentionally acquired throughout its lifetime, but ultimately may affect the objects' condition^[9].

¹⁶ MUHNAC. 2019. Preservation of Historical Chemicals: Basic procedures (internal documentation)

¹⁷ Teixeira, C. personal communication, August 2019.

¹⁸ Accessed at <<https://university-museums-and-collections.net/>> [December 2018].

Table 4.1. Comparison of inherent and acquired characteristics of the different material components present in collections of historical chemicals.

Material	Inherent characteristics	Acquired characteristics
Chemical substances	Chemical substances' physical and chemical properties	Ageing and alteration of chemicals' properties; degradation into toxic or reactive substances; contamination through contact with other chemicals ^[8]
Glass container	Composition, manufacturing techniques, surface features and glass homogeneity ^[32]	History of use; contact with environmental factors, exposure to acidic or alkaline solutions in long-term; generation of micro-climates; propagation of corrosion mechanisms
Labels	Paper/inks quality, manufacture and intrinsic susceptibility to deterioration	Physical and chemical alterations due to history of use; material degradation due to environmental factors

4.1. Preservation guidelines' proposal

The proposal for these guidelines is based on three different phases. First, the criteria for selection of chemicals. This is entirely up to the institutions' desires and what is their purpose for the display or storage of collections of chemicals. The criteria proposed was based on the MUHNAC's internal procedures and experience ¹⁹, but also reflects some aspects found in literature ^[68].

I. Criteria for selection

- Historical significance and value of the chemical, both in regard to its contents, to its container and label (due to its provenance, its history of use, the manufacturer or other relevant factors);
- Representation within the collection;
- Conservation and material conditions of all components;
- Safety to the collection, its caretakers and the public.

II. Collections' care

Following the selection criteria, the first part in the collections' care processes, as will be presented, has to do with general conservation measures. These are the actions that can be taken as the first steps towards the improvement of the preservation of collections. The compiled measures can be found in Table 4.2.

Table 4.2. General conservation measures for the improvement and preservation of collections of historical chemicals.

<p style="text-align: center;">Collection Survey</p> <p>In order to know what exists in the collection and where the objects are located, a survey is a necessity in any collection. It is important to know:</p> <ul style="list-style-type: none"> • Number of objects; • Characteristics (such substance types); • Manufacturers (when applicable); • Location of the objects; • Conservation condition. • Hazards risks 	<p style="text-align: center;">Conservation assessment</p> <ul style="list-style-type: none"> • Problems in conservation should be assessed and documented. If needed, visually identify which objects are at higher risk of deterioration (with a tag or a colouring system); • Evaluate your collection according to scales to define its condition, which objects are priorities and need curative treatment, and which are the materials at largest risk.
<p style="text-align: center;">Inventory and documentation</p> <ul style="list-style-type: none"> • To every object should be added an inventory number and accomplished a description of the item. If applicable, 	<p style="text-align: center;">Photographic documentation</p> <p>Photographic documentation is essential to the collection's preservation. It allows the register</p>

¹⁹ MUHNAC. 2019. Preservation of Historical Chemicals: Basic procedures (internal documentation)

<p>associated documentation should also be included.</p> <ul style="list-style-type: none"> • Inventory numbers should be labelled and with the objects for easy identification. • The results from the conservation assessment should be associated to the inventory database, with date, so that it may be validated in subsequent monitoring. 	<p>of the object's condition as it was found, and can be used to:</p> <ul style="list-style-type: none"> • Follow the progression of any material alteration; • If not labelled, or in the case of loss of inventory tags, a photograph associated to the objects inventory database can be useful to find an object.
<p>Creation of protocols</p> <ul style="list-style-type: none"> • Create protocols for access, handling, safety and disposal of chemicals, and also conservation of the collection. • These protocols should be accessible by all the collections' responsible, caretakers and other institution staff. 	<p>Regular monitoring</p> <p>Objects that have been identified with conservation problems, as well as the collection in general, should be regularly monitored, ideally annually or biannually. Objects that present active deterioration should be monitored more frequently, so preventive measures can be readapted.</p>
<p>Hazardous or radioactive substances</p> <ul style="list-style-type: none"> • Hazardous and toxic substances must be properly identified and labelled. Consult the local regulation agencies regarding the possession of such compounds. • In the case of radioactive substances, these should be measured or separated to avoid points of high radioactivity. 	<p>Historical authenticity</p> <p>Depending on the institutions' purpose, the historical authenticity of the objects may differ. However, whenever possible, keeping the objects in their historical context greatly enlarges the collections' or objects historical significance. This includes original cabinets, traces or marks of use.</p>
<p>Disaster preparedness</p> <p>Create an emergency plan in the case of a disaster – such as fire, flood or natural occurrence. Identify the most liable objects and alert the emergency teams to their existence. If possible, draft a map with routes and exits closest to the object priorities – such as chemicals that may further catalyse the disaster.</p>	<p>Creating a specialized contact list</p> <p>Keep a list of contacts which may be necessary in special cases or occurrences, such as local emergency entities, specialized personnel (chemists, curators, conservators) or containment and management of chemical substances.</p>

Following the presented measures, the next phase is the implementation of preventive conservation measures. This is divided by collection locations (Table 4.3.) and material components (Table 4.4.). Recommendations are made based on the agents of deterioration, as defined by Michalski^[59], and previously explored in the present dissertation that may be relevant to these particular collections.

Table 4.3. Preventive conservation measures applicable to collection locations with collections of historical chemicals.

For collection locations	
<p>Environmental control</p> <p>Environmental control is one of the key aspects to the collections' well-being, as incorrect temperature and relative humidity will influence the processes of degradation of multiple materials.</p> <p>It is recommended that there is minimal fluctuation of temperature and relative humidity, as to not exert strains on the materials or to trigger corrosion or other deterioration mechanisms.</p>	<p>Air quality and contaminants</p> <p>Pollutants and contaminants may enter the collection space either due to external sources, or due to the emission of volatile compounds from display or storage materials, as in the case of wooden cabinets.</p> <p>If the original and historical display/storage of the collection is made of wooden materials, the chemicals should be kept as much as possible within, preserving the authenticity as a whole.</p>

For collection locations	
<p>Temperature fluctuations should not be over 2° to 3°C, and relative humidity fluctuations should be avoided to surpass 5%. Gradual adaptation to seasonal changes should be made ^[48].</p> <p>In the case of old or historic buildings, without HVAC systems and depending on the environmental conditions, portable systems such as dehumidifiers/humidifiers should be used.</p>	<p>Certain chemicals can contaminate materials and rooms due to highly active vapours or smells. If possible, chemical extraction systems should be considered, both for safety and comfort reasons.</p>
<p style="text-align: center;">Lighting conditions</p> <p>Both in display and storage rooms, whenever not necessary, do not leave the lights on. This prevents the unnecessary exposure of materials to photo-effects and light deterioration.</p> <ul style="list-style-type: none"> • If possible, invest in light systems that are UV and IR free – such as LEDs. If not, limit material exposure to lights that may contain high UV contents, or apply UV filters to minimize the risk. • Conservation guidelines for sensitive materials, generally recommend light units at 50-80 lux and below 75µW/lm to avoid the UV radiation damage ^[51] 	<p style="text-align: center;">Integrated Pest Management ^[59,71]</p> <p>In the presence of collections that are rich in organic materials or in uncontrolled environments, pests may start to appear. Some solutions to pests' control may include:</p> <ul style="list-style-type: none"> • Keeping the spaces clean; • Visual monitoring for the presence of pests, nests, eggs, cobwebs, or other products of pest activity; • Using traps for capturing crawling or flying insects, in association with the visual monitoring; • Controlling the storage/exhibition environment; • Consulting a specialist in pest control and management and a conservator for assessment of potential damages.

Table 4.4. Preventive conservation measures applicable to material components that may constitute collections of historical chemicals.

For material components	
<p style="text-align: center;">Environmental control</p> <p>The recommendations previously mentioned from the collection locations, can also be applied to the different material components. Incorrect environments can trigger a multiple of material damages, from the alteration of the chemical substances to increasing glass corrosion risks or accelerating deterioration of paper.</p> <p>Materials that are in active deterioration should be kept at tighter controlled atmosphere. This action is a means to mitigate the advancement of deterioration. In the particular case of chemical objects, fluctuations should be kept even lower.</p>	<p style="text-align: center;">Air quality and contaminants</p> <ul style="list-style-type: none"> • Chemical substances: To prevent the release of potentially harmful or unpleasant odours from the chemicals, consider sealing the stoppers. Avoid irreversible materials, such as silicones, as these materials age, they may become insoluble and irreversible and may cause damage to the containers ^[72]. In doubt, consult a conservator for the proper sealing materials and procedures of the stoppers. • Glass containers: At the suspicion of presence of VOCs, close attention should be taken to the containers, as they may become corroded ^[37]. • Labels: Both acidic agents as well as dust can damage paper labels, and thus should be monitored ^[53]
<p style="text-align: center;">Lighting conditions</p> <p>The recommendations from the collection locations are also applicable, and relevant to</p>	<p style="text-align: center;">Integrated Pest Management</p> <ul style="list-style-type: none"> • Chemical substances: Monitor organic substances that may attract the attention

For material components	
<p>the chemical substances and labels. These are the most sensitive materials and are, therefore, more susceptible to irreversible damage by light.</p>	<p>of pests or biological agents – such as insects, fungi or mould. This can be achieved by keeping the environment at levels that prevents their appearance.</p> <ul style="list-style-type: none"> • Glass containers: Not relevant. • Labels: As most labels are composed of organic materials, these may attract, similarly with chemical substances of organic nature, the presence of pests or biological agents. The same recommendations are therefore applicable.

III. Collections' caretakers

The final section of these guidelines corresponds to the recommendations focused on the collections' caretakers, as presented in Table 4.5.

Table 4.5. Recommended procedures for the collections' caretakers.

General recommendations	Health and safety
<ul style="list-style-type: none"> • For the transport of chemicals, preferably place these in trays or stable trolleys; • Whenever handling chemical containers avoid handling the objects by the neck of the container. Always grab by the base or support by the base and the body of the container. Do not grab containers by the stoppers. 	<ul style="list-style-type: none"> • Always use personal protective equipment (PPE). This should include lab coats and resistant gloves (such as nitrile) at all times. When necessary, eye protection and respiratory masks must be used; • Always be aware of the chemicals that are being handled or conserved. Reading the MSDS of determined compounds is essential to adopt the correct procedure for dealing with a substance. When handling known reactive, toxic or fumigating chemicals, work in a fume hood. Also applicable for chemicals with a poor conservation condition; • In case of accident, report to specialized contact lists – such as in the case of breakage or chemicals spills— and seek for medical attention.

5. Conclusions

Through the development of the present study it was possible to face the inherent challenges that collections of chemicals present. Not only are these large collections, with a multitude of conservation problems, but they also present an inter-relationship between materials, such as the glasses, the nature of the chemicals and the labels, to name the most common materials found.

To assess such a complex collection and respond to these challenges it was necessary to create a multidisciplinary approach, that encompassed both an understanding of the history of science and the materiality of these objects, the way the materials interact with each other and with their surrounding environment, and also which conservation aspects could be improved. Through a scientific approach, the characterization of these materials was used to obtain a deeper understanding of their structures and alterations.

It is with this approach that the present dissertation was developed. The major focus was the glass as it is the most common container material used for the storage of chemicals, both at the MUHNAC's collection, as well as in other collections. This makes the data compiled from studying the MUHNAC's glasses an important contribution to the understanding and preservation of containers made out of glass, present in other collections of historical chemicals.

Through the conservation survey of the MUHNAC's collection, it was possible to gather data on how the collection is composed and what are its particularities. In the conservation assessment of the collection, it was possible to observe that the most concerning corrosion patterns are related to loss of transparency and formation of products at the glass surfaces. The evaluated environments showed that the collections are kept in locations where the values for temperature and relative humidity are within inadequate ranges, as the most concerning aspect is the large fluctuations which influence and can further accelerate the deterioration of the materials. In quantifiable terms, 69,5% of the collection can be found in a good conservation grade. The remainder chemicals found worst conservation conditions are therefore in need of monitoring or immediate conservation actions, to halt deterioration processes and irreversible damage.

The analytical approach, although not providing clear conclusions other than that the glasses appear to be common soda-lime silicate glasses, and are in active processes of chemical alteration, further studies are necessary to continue assessing the active deterioration and corrosion processes of materials that exist in collections from this time frame and typology.

The major conclusion drawn from the study the MUHNAC's collection of historical chemicals is that rather than just intrinsic or external factors, a third important factor that may contribute to the current conservation condition is its history. It is unknown what were the previous conditions that the materials, such as the glasses, the labels or the chemicals were subjected to, and how these have already affected its current conditions. This becomes a weighing factor in the interpretation of the conservation condition, especially if the collections previously had a latency period in which conditions were unknown and scarce documentation is available.

Another input from this study is the valorisation of these collections, both to the contexts of scientific heritage and to historians of science, but also to bring a new perception of collections that are in need of the development of methodologies and guidelines for an effective preservation. This work aimed to fill a gap, that is the lack of preservation guidelines, and that they may be followed and applicable to similar collections. This outcome also aims to shift that paradigm, and not only encourage other interested institutions in the development of their own preservation studies, with their own collections, but also to share the results with the community so that these collections may gain a larger visibility.

To conclude, the major contribution that the present dissertation brings is, firstly, to contribute to generate more information about the MUHNAC's collection of historical chemicals and how its results can be incorporated in its continuous preservation. In a broader scale, this project aimed to provide more evidences for the areas involved in the study of scientific heritage and, most importantly, to the Conservation and Restoration field itself, so that the conservation sciences can embrace scientific heritage as a vulnerable part of heritage.

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Appendix I. MUHNAC's historical chemicals' collection survey (additional information)

Table I.1. Chemicals' companies and manufacturers identified in the collection.

Company name	Number	%
E. Merck	281	14,2
Poulenc-Frères	59	3,0
British Drug Houses	28	1,4
GeHe & Co. A.G.	20	1,0
LaMotte Chemical	19	1,0
May & Baker	16	0,8
Sociedade Zickermann	10	0,5
Shell	9	0,5
Pharmacia Barral	8	0,4
National Aniline Division	7	0,4
Baker's Analyzed	5	0,3
Aktiengesellschaft Hommel's Haematogen	5	0,3
Schering-Kalbaum A.G.	5	0,3
Carl Zeiss Jena	4	0,2
Eastman Kodak Organic Chemicals	4	0,2
Mallinckrodt Chemical Works	3	0,2
Howard & Sons Ltd.	3	0,2
Thomas Tyrer & Co.	2	0,1
The Atlas Chemical Co.	2	0,1
Allen & Hanburys Ltd	2	0,1
J.D. Riedel - E. de Haen A.G. Berlin	2	0,1
Sociedade Industrial Farmacêutica (Laboratórios Azevedos)	2	0,1
Central Scientific Company	2	0,1
Serlabo	2	0,1
M&B Products	2	0,1
Dr. K. Hollborn & Sohne Leipzig	2	0,1
Pestana & Fernandes	2	0,1
Riedel de Haen ag Seelze Hannover	1	0,05
Fisher Scientific	1	0,05
Companhia de Higiene	1	0,05
Robiquet, E. Pelletier & Fontaine	1	0,05
Robiquet, Boyveau, Pelletier	1	0,05
Bayer	1	0,05
Comar & Cie/Laboratoires Clin	1	0,05
Metrohm	1	0,05
H. Trommsdorff	1	0,05
Frederick Allen & Sons	1	0,05
S.B. Pennick & co	1	0,05
T. & H. Smith Ltd	1	0,05
Mètra	1	0,05
Red Star Chemical CO.	1	0,05
Ribeiro da Costa & C ^a	1	0,05
Acheson Colloids Corporation	1	0,05
DIFCO Laboratories	1	0,05
Stanford, Allen & Sons Ltd	1	0,05
Johnson, Matthey & Co. Ltd	1	0,05

Company name	Number	%
Gunther Wagner Hanover	1	0,05
Dr. Theodor Schudhart, G.m.b.H. Chemische Fabrik	1	0,05
William & Bros, Ltd.	1	0,05
Farmácia Albano	1	0,05
V. Reis Lds	1	0,05
Dr. G. Grubler & Co.	1	0,05
Phoenix Chemical Works - Frederick, Allen & Sons	1	0,05
Biosynth Pharmaceutical/ Manufacturing Chemists Maspeth New York	1	0,05
James Hudson Co.	1	0,05
C.F. Boehringer & Soehne	1	0,05
Carlo Erba	1	0,05
C.A.F. Kahlbaum Chemische Fabrik	1	0,05
Lindsay Chemical Company	1	0,05
TOTAL (in relation to the collection)	604	30,6%

Table I.2. Toxic chemicals and hazardous compounds identified in the collection.

Chemical compounds	Number	%
Cyanides	47	2,4
Mercury	40	2,0
Lead	33	1,7
Arsenic	14	0,7
Cadmium	11	0,6
TOTAL (in relation to the collection)	145	7,4%

Appendix II. Case-study: Portable set of chemicals for chemical analysis



Figure II.1. Portable set of chemicals for chemical analysis, chosen as a case-study for the analytical study of the present dissertation. Photograph © MUHNAC, Ana Rita Lourenço, 2018.

Table II.1. Information compiled through the MUHNAC's database. Object's inventory made by Eugénia Fronteira e Silva, MUHNAC's volunteer. English translation and minor alterations performed by the author.





















Inventory number	MUHNAC/UL588
Designation	Portable set of chemicals for chemical analysis
Description	<p>Wooden box for the storage and transport of chemicals. It opens to reveal a laddered shelf effect, in which 75 holes are found for the placement of the chemicals' containers. Outside it has two drawers with 4 rounded knobs and on the sides, it has two lateral handles for transportation.</p> <p>It contains 55 large colourless glass containers (UL000588/1 to 5888/24, UL000588/26 to UL000588/35, UL000588/37 to UL000588/57) and 19 small containers, 18 of which are colourless (UL000588/35, UL000588/36, UL000588/58 a UL000588/73) and 1 amber coloured (UL000588/74).</p>
Entry	Entered into the museum, as an incorporation, included into the old fund – objects that belonged to the space before it was musealized – by Professor Alzira Almoester Ferreira, Vice-Director of the Museum of Science of the University of Lisbon at the time of entry.
Dimensions	<p>Wooden box Length: 100,00 cm Width: 51,00 cm Height: 41,00 cm</p> <p>Large glass containers Height: 17,00 cm Diameter: 6,30 cm</p> <p>Small glass containers Height: 12,50 cm Diameter: 4,30 cm</p>

Table II.2. List of chemical substances stored inside the glass containers of the portable set of chemicals. Chemicals' nomenclature has been translated to English by the author, presenting also the original nomenclature in *italic* as written in the glass labels. GHS pictograms were added to each chemical identified; plus, analytical techniques employed per item

Inventory n. °	Chemical	Analysis	Inventory n. °	Chemical	Analysis
UL000588/1	Sodium borate <i>Borato de Sodio</i>	p-XRF	UL000588/24	Ammonium carbonate <i>Carb.º de Ammonio</i>	p-XRF
UL000588/2	Zinc sulphate <i>Sulf.to de Zinco</i>	p-XRF ICP-AES HPIC	UL000588/25	Manganese chloride <i>Chloreto Mangan:</i>	p-XRF ICP-AES HPIC
UL000588/3	Potassium nitrite <i>Azotito de Potassio</i>	p-XRF	UL000588/26	Sodium bitartrate <i>Tartrato Acido de Sodio</i>	p-XRF
UL000588/4	Hydrochloric acid <i>Acido Chlorhydrico</i>	p-XRF	UL000588/27	Potassium chlorate <i>Chlor.to de Potassio</i>	p-XRF
UL000588/5	Ammonium oxalate <i>Oxalato de Ammonio</i>	p-XRF	UL000588/28	Ammonium aluminum sulfate <i>Alumen Ammoniacal</i>	p-XRF
UL000588/6	Potassium arsenite <i>Arseni.º de Potassio</i>	p-XRF	UL000588/29	Sodium thiosulfate <i>Hyposulfito de Sodio</i>	p-XRF
UL000588/7	Sodium acetate <i>Acét.º de Sodium</i>	p-XRF	UL000588/30	Ferric chloride <i>Chlor.ºe Ferrique</i>	p-XRF
UL000588/8	Potassium bromide <i>Brometo de Potassio</i>	p-XRF	UL000588/31	Potassium iodide <i>Yodeto de Potassio</i>	p-XRF
UL000588/9	Bismuth nitrate <i>Acetato Acido Bismut:</i>	p-XRF	UL000588/32	Sodium nitroferricyanide <i>Nitratopruss.º de Sodio</i>	p-XRF
UL000588/10	Barium chloride <i>Chlor.º de Bario</i>	p-XRF	UL000588/33	Potassium chromate <i>Chromato de Potassio</i>	p-XRF
UL000588/11	Ammonia <i>Ammoniaque</i>	p-XRF	UL000588/34	Cobalt nitrate <i>Azot.ºe de Cobalt</i>	p-XRF

Inventory n. °	Chemical		Analysis	Inventory n. °	Chemical		Analysis
UL000588/12	Strontium chloride <i>Chloreto Stroncio</i>		p-XRF ICP-AES HPIC	UL000588/35	Magnesium sulfate <i>Sulf:te de Magnésium</i>	-	p-XRF ICP-AES HPIC
UL000588/13	Platinum chloride <i>Chlor:re de Platinum</i>		p-XRF	UL000588/36	Chromium chloride <i>Chloreto Chromo</i>		p-XRF
UL000588/14	Carbon sulfide <i>Sulfureto de Carbono</i>		p-XRF	UL000588/37	Ammonium chloride <i>Chlorhydr:te d'Amm:que</i>		p-XRF
UL000588/15	Oxalic acid <i>Acido Oxalico</i>		p-XRF	UL000588/38	Sodium sulfite <i>Sulfito de sodio</i>		p-XRF
UL000588/16	Sodium sulphate <i>Sulfato de Sodio</i>	-	p-XRF ICP-AES HPIC	UL000588/39	Potassium ferrocyanide <i>Ferro-cyan:to de Potassio</i>		p-XRF
UL000588/17	Ammonium molybdate <i>Molybd:to de Ammonio</i>		p-XRF	UL000588/40	Potassium perchlorate <i>Perchlor:to de Potassio</i>		p-XRF
UL000588/18	Chloroform <i>Chloroformio</i>		p-XRF	UL000588/41	Sodium arsenate <i>Arsen:ato de Sodio</i>		p-XRF
UL000588/19	Potassium bichromate <i>Bichromato de Potassio</i>		p-XRF	UL000588/42	Potassium ferricyanide <i>Ferri-cyan:to de Potassio</i>	-	p-XRF
UL000588/20	Calcium chloride <i>Chlor:to de Calcio</i>		p-XRF ICP-AES HPIC	UL000588/43	Potassium thiocyanide <i>Sulfocyan:to de Potassio</i>		p-XRF
UL000588/21	Ether <i>Ether</i>		p-XRF	UL000588/44	Lead nitrate <i>Azotato de Chumbo</i>		p-XRF

Inventory n. °	Chemical	Analysis	Inventory n. °	Chemical	Analysis
UL000588/22	Mercury chloride <i>Chlor.:^{re} Mercurique</i>	p-XRF	UL000588/45	Tartaric acid <i>Acido Tartrico</i>	p-XRF
UL000588/23	Potassium chlorate <i>Chlorato de Potassio</i>	p-XRF	UL000588/46	Sulfurous acid <i>Acido Sulfuroso</i>	p-XRF
UL000588/47	Copper sulfate <i>Sulf.:^{to} de Cobre</i>	p-XRF	UL000588/61	Potassium iodate <i>Iodato de Potassio</i>	p-XRF
UL000588/48	Potassium silicate <i>Silicato de Potassio</i>	p-XRF	UL000588/62	Mercury bichloride <i>Bichlor.:^{to} Mercurio</i>	p-XRF
UL000588/49	Ammonium hydrosulfide <i>Sulfhydr.:^{to} Ammoniaco</i>	p-XRF	UL000588/63	Nickel sulphate <i>Sulfato de Nikel</i>	p-XRF
UL000588/50	Ammonium chloride <i>Chlor.:^{to} de Ammonio</i>	p-XRF	UL000588/64	Magnesium mixture <i>Mistura Magnes:</i>	p-XRF
UL000588/51	Sodium phosphate <i>Phosph.:^{to} de Sodio</i>	p-XRF ICP-AES HPIC	UL000588/65	Lithium chloride <i>Chloreto Lythio</i>	p-XRF ICP-AES HPIC
UL000588/52	Nitric acid <i>Acido Azotico</i>	p-XRF	UL000588/66	Antimony trichloride <i>Trichlor.:^{to} de Antim:</i>	p-XRF
UL000588/53	Aqueous chlorine <i>Agua de Chloro</i>	p-XRF	UL000588/67	Platinum chloride <i>Chloreto de Platina</i>	p-XRF
UL000588/54	Potassium nitrate <i>Azotato de Potassio</i>	p-XRF	UL000588/68	Aluminum sulphate <i>Sulfato de Aluminio</i>	p-XRF
UL000588/55	Sodium hexafluorosilicate <i>H.:^{ro} Fluo-Silic.:^{to} de Sodio</i>	p-XRF	UL000588/69	Mercury nitrate <i>Nitrato Mercurioso</i>	p-XRF

Inventory n. °	Chemical		Analysis	Inventory n. °	Chemical		Analysis
UL000588/56	Sulfuric acid <i>Acido Sulfurico</i>		p-XRF	UL000588/70	Antimony pentachloride <i>Pentachlor:to de Antim:</i>	 	p-XRF
UL000588/57	Lithium chloride <i>Chlor:oe de Lithium</i>		p-XRF	UL000588/71	Cadmium sulphate <i>Sulfato de Cadmio</i>	 	p-XRF
UL000588/58	Gold chloride <i>Chloreto de Ouro</i>		p-XRF	UL000588/72	Cobalt nitrate <i>Azotato de Cobalto</i>	   	p-XRF
UL000588/59	Gold chloride <i>Chloreto de Ouro</i>		p-XRF	UL000588/73	Nessler's reagent <i>Reagente de Nessler</i>	  	p-XRF
UL000588/60	Tin chloride <i>Chloreto Estanico</i>		p-XRF	UL000588/74	Silver nitrate <i>Azotato de Prata</i>	   	p-XRF

Appendix III. Equipment and Analytical Conditions

- Stereomicroscope observations

Observations were carried out using a Leica M165 C stereo microscope with a 16.5:1 zoom, 7.3x to 120x magnification and up to 906 lp/mm resolution. Image capture was performed using the coupled digital microscope camera Leica DMC4500. This camera holds a megapixel CCD sensor, with live image speed of up to 18 frames per second and SXGA resolution of 1280 x 960 pixels. Image processing was carried out in the Leica Application Suite X, allowing the acceleration of image visualization, enhancement, measurements, documentation and the archival of pictures.

- Portable X-Ray Fluorescence Spectrometer

p-XRF analyses were carried out using a Bruker S1 Titan Model 600, equipped with a Fast SDD detector of typical resolution of <145eV. The excitation source is a Rhodium (Rh) target X-ray tube of 4W. Maximum voltage is 50kV and 100µA. Elemental range goes from Magnesium (Mg) to Uranium (U). It also includes a detector shield and color CMOS camera for visualization of the analyzed sample. The samples were analyzed using the integrated acquisition mode GeoExploration, optimized for the detection and analysis of minerals and oxides. Limits of detection are present in Table III.1. The GeoExploration mode operates at a 3-phase analysis, totaling 90s of acquisition time. Phase 1 reads at 30kV, 26µA, phase 2 reads at 50kV, 26µA and phase 3 reads at 15kV, 26µA, with 30s of acquisition on each phase (Table III.2).

The samples were measured 3 times and an average was calculated. Automatic quantification is performed within the Bruker Elemental S1 proprietary software. Elements not automatically presented as oxides were converted through oxide factors.

Corning Museum of Glass standards CMOG A and CMOG B were analyzed to compare to the samples' composition and calculate relative accuracy of the detected elements, according to the following equation:

$$\text{Relative Accuracy} = \frac{\text{Glass standard composition} - \text{Measured composition}}{\text{Glass standard composition}} \times 100$$

Table III.1. Limits of detection (LOD) for some of the elements most relevant to the analysis. Oxides marked with (*) are defaulted to report as oxide.

Element/ Oxide	MgO*	Al ₂ O ₃ *	SiO ₂ *	P	S	Cl	K ₂ O*	Ca	Ti	Mn	Fe	As	Pb	Ba	Sb	Zr
LOD (ppm)	4100	1240	NA	38	63	124	55	33	40	11	20	2	4	42	21	3

Note: Actual Limit of Detection in a sample is dependent on several factors such as: Matrix interferences, Overlapping elements, level of statistical confidence and testing time.

Table III.2. Phases and element detection using the GeoExploration calibration.

Phase & Voltage	Acquisition time (total 90s)	Elements detected
Phase 1 (30kV)	30s	K, Ca, Ti , V, Cr, Mn, Fe , Co, Ni, Cu, Zn , Ga, Se, Hf, Ta, W, Au, Tl
Phase 2 (50kV)	30s	As , Se, Rb, Sr , Y, Zr , Nb, Mo, Rh, Pd, Ag, Cd, In, Sn, Sb , Te, Ta, Pt, Au, Hg, Tl, Pb , Bi, Ce, Th, U
Phase 3 (15kV)	30s	Mg, Al, Si , P, S, Cl, K, Ca

- Inductively Coupled Plasma Atomic Emission Spectroscopy

ICP-AES analysis were carried out using a Horiba Jobin-Yvon equipment, model Ultima, of radial observation, equipped with a RF generator of 40,68MHz and a Czerny-Turner type monochromator of 1,00m. Samples were analyzed at a 1050kW potency, Argon Plasma flow of 12,0L/min, with a 0,3L/min Argon flow coating. The diameter of the injector tube is 3mm. The nebulizer is a Mira Mist, with a cyclonic nebulization chamber, at a 3bar pressure. Pump velocity was 17 rpm.

Data acquisition and equipment control are carried out through the computer with the JY v.5.4 software, allowing on-line visualization of all parameters and data obtained.

The samples were diluted into 1:100 and 1:1000 proportions to allow a better reading of all elemental concentration in the case of highly concentrated samples. Dilution was performed using deionized water, which was also submitted to analysis, so the added water values could be removed in the quantification process.

- High Performance Ionic Chromatography

HPIC analysis were performed in a DIONEX ICS3000, with a Thermo Ionpac AS91-HC 250x4mm + AG9HC column. The eluent used was a 9mM of Na₂CO₃ injected at 1,0ml/min, at T°C 25. Analyses was performed on samples prepared into liquid form, diluted in a 1:100 proportion and injected. A calibration standard was used, consisting of a mixture of fluorite, chloride, nitrite, bromide, nitrate, phosphate and sulphate.

- pH measurements

For the glass surfaces: pH measurements were carried out using a Crison PH25, with a flat-head electrode, and calibrated with two Crison buffer solutions (pH=4 and pH=7) at a temperature of 26°C.

For the chemical solutions: pH measurements were carried out using a Sartorius Docu-Meter, with a MicroTrode electrode, and calibrated with prepared pH=4 and pH=7 buffers at a temperature of 21°C.

- Relative Humidity and Temperature Dataloggers

Relative Humidity (HR/%) and Temperature (T/°C) measurements were carried out using a Rotronic HygroLog, Art NO: HL-20D, equipped with AirChip Technology. Data was worked and downloaded in the Rotronic HW4 software.

- Light meter

Light measurements were carried out using a portable Delta OHM HD2302.0 Light Meter, equipped with an LP471 P-A two sensors combined probe with a SICRAM module for measuring illuminance (Lux), with standard photopic spectral response, and irradiance ($\mu\text{W}/\text{cm}^2$) in the UVA spectral range (315-400nm, with peak at 360nm). Although, the probe provides the ratio of UVA irradiance and illuminance in $\mu\text{W}/\text{lumen}$ – the light measure unit of interest in the museums field. Both sensors are equipped with a diffuser for the correction according to the cosine law.

- Formaldehyde Detector

Formaldehyde detections were carried out using a portable PPM Formaldemeter™ -htV-m, from PPMTechnology Ltd. The instrument's sampling method is through a 10ml snatch-sample of air taken by an internal pump. The acquisition time was 60s per measurement, in the high accuracy mode. The formaldehyde sensor is electrochemical, with a 0-10ppm standard, a 0,01ppm resolution and 10% accuracy at 2ppm.

Appendix IV. Environmental data and measurements

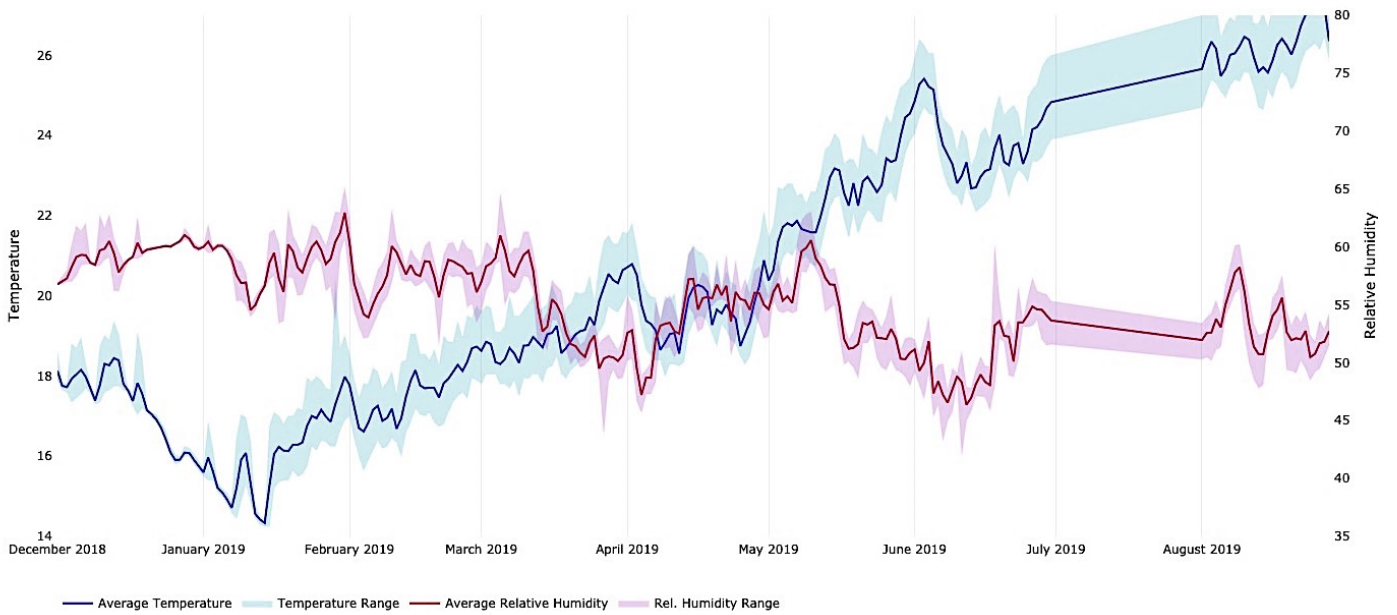


Figure IV.1. Relative humidity and temperature averages and ranges in the Chemistry Visible Storage chemicals' cabinet. Data from December 2018 to August 2019.

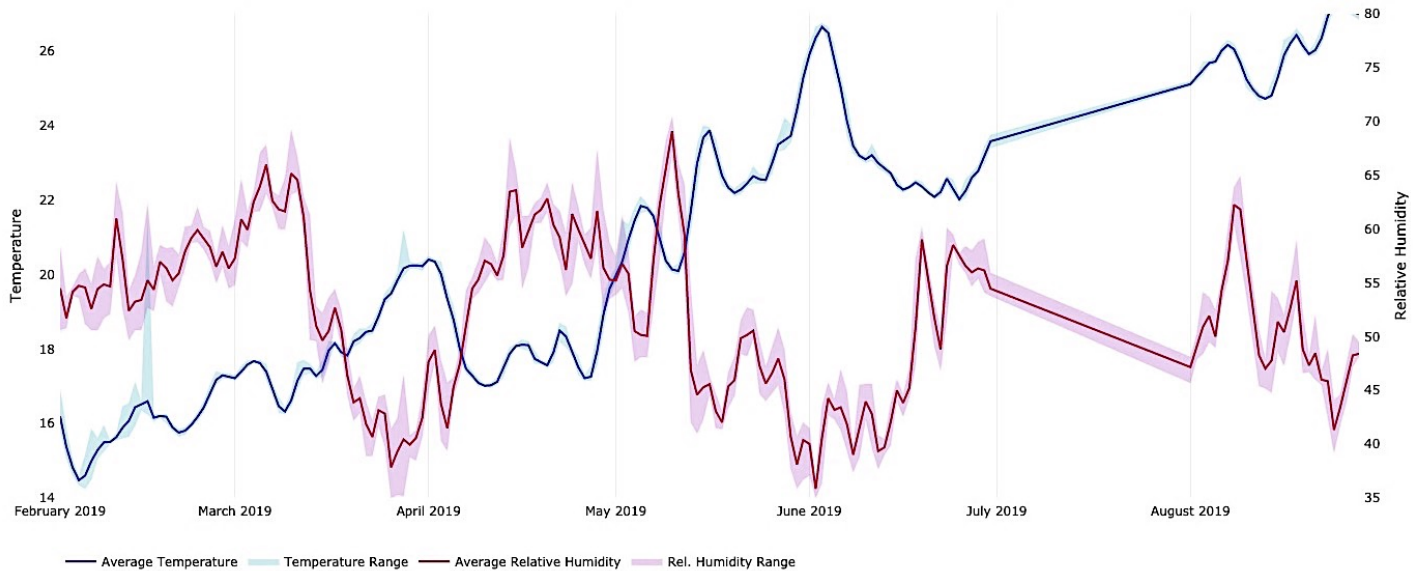


Figure IV.2. Relative humidity and temperature averages and ranges in the Technical Storage chemicals' section. Data from February to August 2019

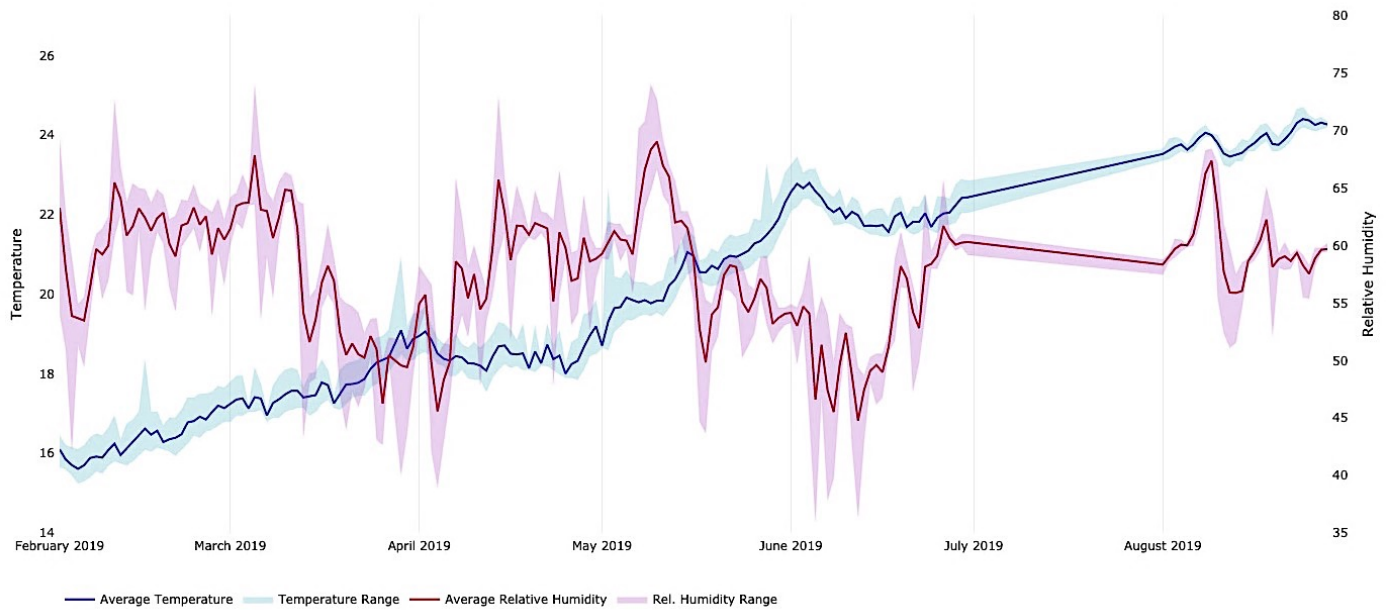


Figure IV.3. Relative humidity and temperature averages and ranges in the Laboratorio Chimico permanent exhibition’s chemicals’ cabinet. Data from December 2018 to August 2019

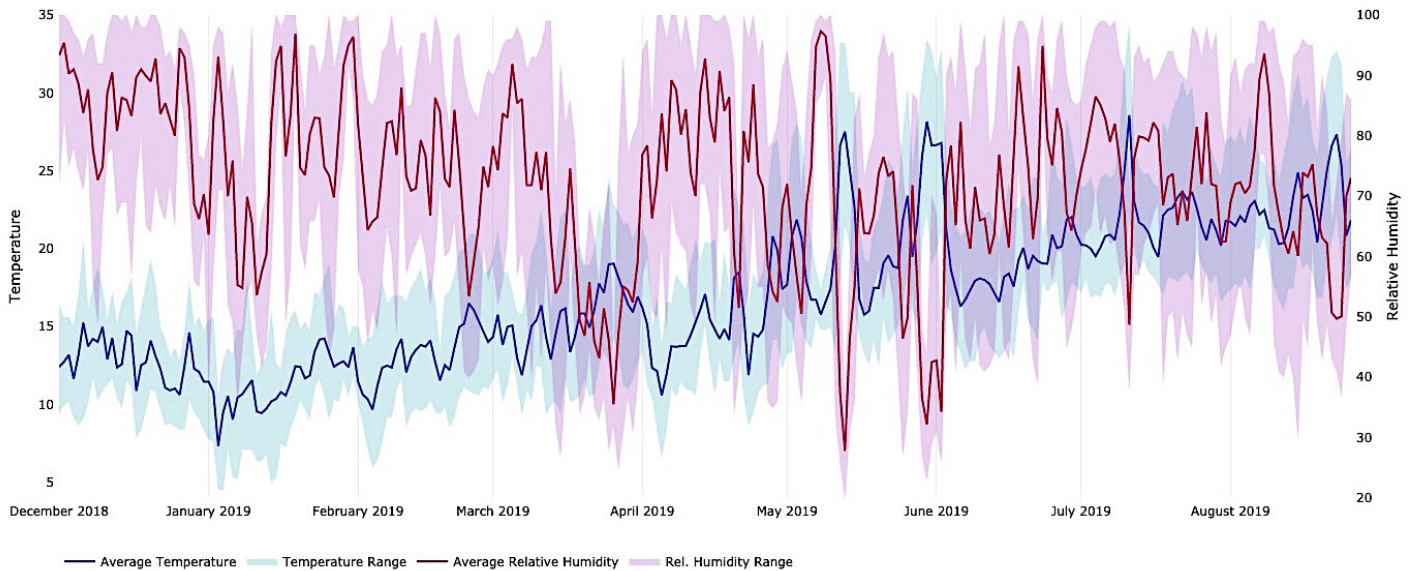


Figure IV.4. Relative humidity and temperature averages and ranges from the IDL external meteorological station. Data from December 2018 to August 2019.

Table IV.1. Data compiled of relative humidity and temperature from the selected collection locations, compared with external data (HR/T) obtained from the IDL meteorological station.

Months	Data	Museum interior						Museum exterior	
		Visible Storage Chemicals' cabinet		<i>Laboratorio Chimico</i> Chemicals' cabinet		Technical Storage Chemicals' section		Meteorological station	
		T (°C)	RH (%)	T (°C)	RH (%)	T (°C)	RH (%)	T (°C)	RH (%)
Dec. 2018	Min.	15,7	56,2	No data				8	49
	Max.	19,4	62,8					20	100
	Average	17,3±0,9	59,3±1,3					12,9±1,3	84,9±7,8
Jan. 2019	Min.	14,3	53,4	No data				3	36
	Max.	20,4	65,1					19	100
	Average	16,0±1,1	58,7±2,2					11,4±1,6	77,0±12,9
Feb. 2019	Min.	15,7	51,6	15,3	42,3	14,3	49,7	6	40
	Max.	19,8	63,2	18,4	72,6	21,5	64,3	21	100
	Average	17,6±0,8	57,2±2,0	16,4±0,6	60,5±3,8	16,0±0,8	55,8±2,8	13,1±1,7	73,5±8,4
Mar. 2019	Min.	17,5	43,9	16,8	40,1	16,3	35,0	9	25
	Max.	19,8	64,6	20,9	73,9	21,2	69,2	24	99
	Average	17,6±0,9	54,6±3,8	17,7±0,6	56,7±6,6	18,1±1,0	51,6±9,6	15,5±1,7	63,4±15,1
Apr. 2019	Min.	18,0	45,7	17,6	39,0	17,0	39,4	7	34
	Max.	22,1	60	19,9	72,9	20,5	68,4	27	100
	Average	19,6±0,8	54,0±2,9	18,5±0,4	57,6±5,2	18,1±1,0	56,0±6,2	15,1±2,4	75,9±11,6
May 2019	Min.	19,8	48	18,6	43,7	19,8	35,9	13	20
	Max.	25,5	63	23,3	74,0	25,7	70,4	33	100
	Average	22,5±1,1	54,6±3,2	20,5±0,9	59,0±5,2	22,2±1,4	50,2±7,8	20,4±1,8	63,1±18,2
Jun. 2019	Min.	22,1	42	21,5	36,0	22,0	35,0	12	26
	Max.	26,4	60,1	23,5	65,6	26,8	60,1	33	100
	Average	23,9±1,0	50,6±3,1	22,1±0,4	53,5±5,5	23,4±1,4	47,7±7,3	19,4±2,5	70,4±12,5
Jul. 2019	Min.	23,6	47,1	22,1	51,0	23,6	42,7	16,6	38
	Max.	27,3	59,9	24,9	66,6	26,6	62,2	34	99
	Average	25,5±0,8	55,7±2,0	23,3±0,6	62,9±2,3	25,1±0,9	54,5±3,8	21,8±1,9	74,7,0±8,2
Aug. 2019	Min.	24,7	47,8	23,2	51,1	24,7	39,2	16,1	30
	Max.	28,2	60,2	24,7	68,4	27,7	64,9	33	99
	Average	26,3±0,8	53,2±2,4	23,9±0,3	59,8±3,1	26,0±0,8	50,4±5,1	22,7±1,9	69,1±10,8

Table IV.2. Average values for the light measurements for the selected collection locations.

Collection spaces		Measurements			
		Lux	$\mu\text{W}/\text{cm}^2$	$\mu\text{W}/\text{lm}$	
Chemistry Visible storage	Chemicals' cabinet, 1 st door from the right	1 st shelf	$29,0 \pm 1,8$	$0,01 \pm 0,00$	3 ± 0
		2 nd shelf	$38,3 \pm 0,7$	$0,04 \pm 0,01$	3 ± 2
		3 rd shelf	$50,3 \pm 0,4$	$0,03 \pm 0,00$	5 ± 1
		4 th shelf	$57,2 \pm 2,0$	$0,05 \pm 0,02$	9 ± 2
	Chemicals' cabinet, 2 nd door from the right	1 st shelf	$20,7 \pm 0,2$	$0,01 \pm 0,00$	4 ± 0
		2 nd shelf	$43,6 \pm 1,4$	$0,02 \pm 0,00$	4 ± 0
		3 rd shelf	$61,7 \pm 2,6$	$0,04 \pm 0,00$	5 ± 1
	Chemicals' cabinet, 3 rd door from the right	1 st shelf	$43,5 \pm 3,4$	$0,02 \pm 0,01$	3 ± 1
		2 nd shelf	$72,6 \pm 0,4$	$0,04 \pm 0,01$	5 ± 1
		3 rd shelf	$51,3 \pm 1,5$	$0,02 \pm 0,00$	4 ± 1
	Chemicals' cabinet, 4 th door from the right	1 st shelf	$35,9 \pm 3,8$	$0,01 \pm 0,00$	1 ± 1
		2 nd shelf	$50,0 \pm 0,9$	$0,01 \pm 0,01$	2 ± 2
	Central bench	Portable set of chemicals (UL000588)	$34,5 \pm 4,2$	$0,01 \pm 0,01$	3 ± 3
Laboratorio Chimico	Chemicals' cabinet	3 rd shelf	$16,2 \pm 0,2$	$0,02 \pm 0,01$	4 ± 3
Technical Storage	Chemicals' rack 1	1 st shelf	$96,8 \pm 6,2$	$0,09 \pm 0,02$	9 ± 1
		2 nd shelf	$50,4 \pm 9,5$	$0,03 \pm 0,01$	6 ± 1
	Chemicals' rack 2	1 st shelf	$143,3 \pm 1,5$	$0,08 \pm 0,01$	5 ± 0
		2 nd shelf	$119,5 \pm 2,1$	$0,09 \pm 0,00$	8 ± 1

Table IV.3. Formaldehyde concentration in the wooden cabinets where a part of the collection is stored.

Location		Formaldehyde concentration
Visible storage	Chemicals' cabinet 1 st door from the right (3 measurements)	0,01ppm
	Laboratorio Chimico Chemicals' cabinet	

Appendix V. p-XRF data analysis

A data analysis approach was performed with the data collected from p-XRF, as a way to assess the quality and confidence of the results achieved from the automatic quantifications generated through the portable equipment software.

Each p-XRF analyses performed in the GeoExploration calibration mode creates a file with the 3 spectra obtained at the different operational energies. Due to the large sample number of analysed objects, 18 were selected to obtain areas of the peaks in the spectra. These were selected by being the 9 glass containers that had been chosen for sample selection for the ICP-AES analyses, and the remaining 9 were chosen, based on the ones with the most different results in the automatic quantifications. Each sample was measured 3 times in order for the automatic quantification to be generated from the measurements' average. Taking in account that each measurement produces 3 different spectra, a total of 156 peak areas were determined.

Peak areas were obtained using the WinaxilBatch pack Canberra, in which the mathematical model for this program uses the method for least squares fitting, in which an algebraic function is used to model the measured spectrum. The peak area is obtained through the spectrum deconvolution and the area considered for each element is the result of an integration of the several fluorescence lines for that element. The WinaxilBatch pack allows for the deconvolution of large amounts of X-Ray spectra ^[1-2].

Further data analysis was accomplished using the software RStudio.

In order to understand the structure of the peak area values of the obtained elements, a Principal Component Analysis (PCA) was applied. This is a widely used method (a linear orthogonal transformation) which yields directions of maximum variance. For this reason, this method is broadly used for dimension reduction, given that the directions that explain a greater data variance are the ones that better describe the data.

Each new direction will be composed by the original input variables, and this is why it is possible to reason about the importance of a given variable in a specific dimension.

For example, if the first dimension explains 70% of the data variability, and in this dimension the variable A accounts for 80% of that dimension, then we can say that the variable A is the variable that most explains the data variability (therefore, the most important variable) ^[3].

The WinAxil data was normalized by using the Fe peak areas, as this is the element that presented least variation between spectra peak areas in all the samples and therefore, the best candidate for data normalization. The PCA was applied to this normalized data.

After the transformation of the data using the PCA (for the 18 objects), an hierarquical cluster technique was performed to understand the group structure of the data in this new space (the PCA space) which can be seen in Figure VI.1.

A plot for the same 18 objects was generated for the p-XRF automatic quantification data, can be found in Figure VI.2.

The WinAxil PCA transformation and the p-XRF PCA transformation can explain the data variability with only the two first principal components. WinAxil's PCA explains 92.5%, while p-XRF's explains 98.7%. It is possible to understand that, by analysing both figures VI.1 and VI.2 the data presents the same structure - in spaces that explain more than 90% of the data.

Therefore, it is possible to say that there is a relation between the peak area values and the automatic quantification performed by the p-XRF.

When applying the PCA transformation on the p-XRF data for all the objects – Figure VI.3 -, and comparing with Figure VI.2, it is possible to note that the same groups are shown.

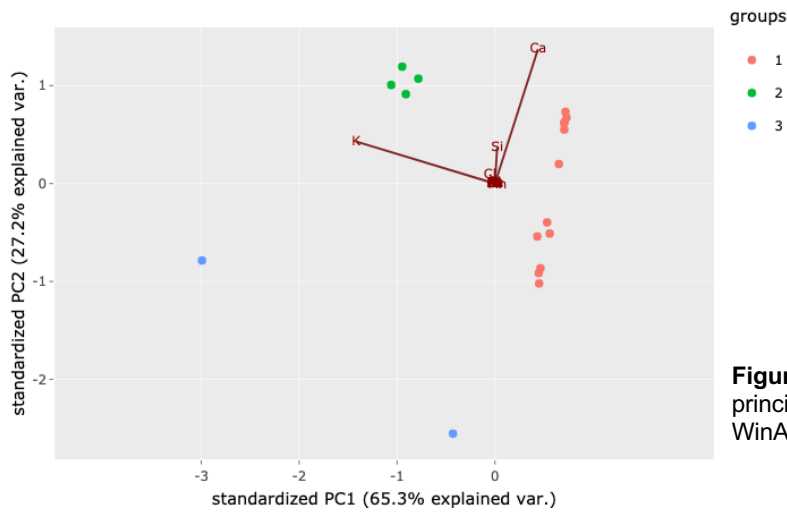


Figure V.1. Scatter plot of the first two principal dimensions of the PCA applied to WinAxil peak area data.

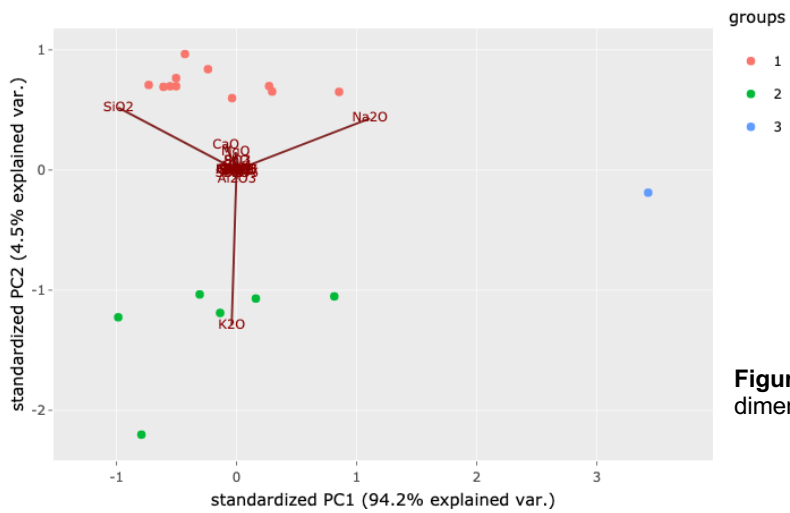


Figure V.2. Scatter plot of the first two principal dimensions of the PCA applied to p-XRF data.

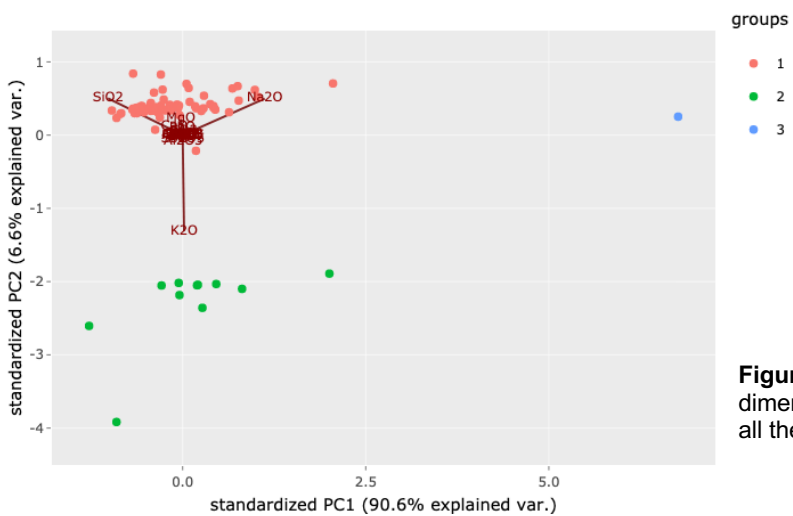


Figure V.3. Scatter plot of the first two principal dimensions of the PCA applied to p-XRF data of all the 74 measured glass containers.

Table V.1. PCA importance of all elements and oxides and data variability, in relation to all the figures presented.

PCA Importance for the Fig. VI.1 plot		PCA Importance for the Fig. VI.2 plot		PCA Importance for the Fig. VI.3 plot	
Explains 92,5% of the data variability		Explains 98,7% of the data variability		Explains 97,2% of the data variability	
Elements	Importance	Oxides	Importance	Oxides	Importance
K	0,4275	K ₂ O	0,2989	K ₂ O	0,2923
Ca	0,4160	Na ₂ O	0,2750	Na ₂ O	0,2735
Si	0,1055	SiO ₂	0,2569	SiO ₂	0,2536
Cl	0,0306	CaO	0,0513	MgO	0,0498
S	0,0079	MgO	0,0346	CaO	0,0376
Mn	0,0079	PbO	0,0179	PbO	0,0376
Fe	0,0017	Al ₂ O ₃	0,0173	Al ₂ O ₃	0,0189
Al	0,0011	SO ₃	0,0169	SO ₃	0,0141
Ti	0,0008	BaO	0,0072	Sb ₂ O ₅	0,0112
P	0,0007	Cl	0,0067	Cl	0,0091
Cr	0,0001	Sb ₂ O ₅	0,0066	MnO	0,0059
Pb	0,0000	MnO	0,0057	BaO	0,0041
As	0,0000	ZrO ₂	0,0027	As ₂ O ₅	0,0029
Ni	0,0000	TiO ₂	0,0008	ZrO ₂	0,0022
Zr	0,0000	P ₂ O ₅	0,0005	P ₂ O ₅	0,0010
Sn	0,0000	As ₂ O ₅	0,0005	TiO ₂	0,0008
Cu	0,0000	Fe ₂ O ₃	0,0003	Fe ₂ O ₃	0,0003
Sr	0,0000	SnO ₂	0,0001	ZnO	0,0001
		ZnO	0,0001	SnO ₂	0,0001
		SrO	0,0000	Cr ₂ O ₃	0,0000
	----	Cr ₂ O ₃	0,0000	CuO	0,0000
		CuO	0,0000	SrO	0,0000
		NiO	0,0000	NiO	0,0000

References:

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- [3] Jolliffe, I.T. ed. 2002. *Principal Component Analysis*, 2nd ed. New York: Springer-Verlag

Appendix VI. p-XRF automatic quantifications

Table VI.1. Composition of all the samples analysed through p-XRF, divided into the groups defined by the PCA analysis. Values in weight percent of oxides (wt%). Na₂O values are obtained through the sum of all components, including residuals, minus 100.

Groups	Samples	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	Cl	K ₂ O	CaO	TiO ₂	MnO	Fe ₂ O ₃	As ₂ O ₃	PbO	BaO	Sb ₂ O ₅
1	588/1	10,0 ±1,0	2,0 ±1,0	0,0 ±0,2	78,6 ±0,8	0,1 ±0,0	0,7 ±0,0	0,1 ±0,0	0,2 ±0,0	7,6 ±0,0	0,0 ±0,0	0,1 ±0,0	0,0 ±0,0	0,1 ±0,0	0,3 ±0,0	0,0 ±0,0	0,2 ±0,0
	588/2	11,3 ±1,0	1,4 ±1,0	0,0 ±0,2	77,9 ±0,7	0,1 ±0,0	0,6 ±0,0	0,1 ±0,0	0,2 ±0,0	7,7 ±0,0	0,0 ±0,0	0,1 ±0,0	0,0 ±0,0	0,1 ±0,0	0,3 ±0,0	0,0 ±0,0	0,2 ±0,0
	588/3	9,9 ±1,0	1,7 ±1,0	0,0 ±0,2	78,4 ±0,7	0,1 ±0,0	1,0 ±0,0	0,1 ±0,0	0,2 ±0,0	7,7 ±0,0	0,0 ±0,0	0,1 ±0,0	0,0 ±0,0	0,1 ±0,0	0,3 ±0,0	0,0 ±0,0	0,2 ±0,0
	588/4	8,7 ±1,0	1,9 ±1,0	0,0 ±0,2	79,3 ±0,8	0,1 ±0,0	1,0 ±0,0	0,1 ±0,0	0,3 ±0,0	7,8 ±0,0	0,0 ±0,0	0,1 ±0,0	0,0 ±0,0	0,1 ±0,0	0,3 ±0,0	0,0 ±0,0	0,2 ±0,0
	588/5	9,1 ±1,0	2,0 ±1,0	0,0 ±0,2	79,1 ±0,8	0,1 ±0,0	0,9 ±0,0	0,1 ±0,0	0,2 ±0,0	7,8 ±0,0	0,0 ±0,0	0,1 ±0,0	0,0 ±0,0	0,1 ±0,0	0,3 ±0,0	0,0 ±0,0	0,2 ±0,0
	588/6	14,8 ±0,9	0,9 ±0,9	0,0 ±0,2	75,3 ±0,7	0,0 ±0,0	1,2 ±0,0	0,0 ±0,0	0,2 ±0,0	6,6 ±0,0	0,0 ±0,0	0,1 ±0,0	0,0 ±0,0	0,2 ±0,0	0,4 ±0,0	0,0 ±0,0	0,2 ±0,0
	588/8	11,7 ±0,9	1,7 ±0,9	0,0 ±0,2	77,1 ±0,7	0,1 ±0,0	0,7 ±0,0	0,0 ±0,0	0,2 ±0,0	7,6 ±0,0	0,0 ±0,0	0,1 ±0,0	0,0 ±0,0	0,1 ±0,0	0,3 ±0,0	0,0 ±0,0	0,2 ±0,0
	588/9	14,7 ±0,9	1,4 ±0,9	0,0 ±0,2	74,4 ±0,7	0,1 ±0,0	1,1 ±0,0	0,1 ±0,0	0,2 ±0,0	7,1 ±0,0	0,0 ±0,0	0,1 ±0,0	0,1 ±0,0	0,2 ±0,0	0,4 ±0,0	0,0 ±0,0	0,2 ±0,0
	588/10	17,9 ±0,9	1,3 ±0,9	0,0 ±0,2	72,0 ±0,7	0,1 ±0,0	1,0 ±0,0	0,0 ±0,0	0,2 ±0,0	6,8 ±0,0	0,0 ±0,0	0,1 ±0,0	0,0 ±0,0	0,1 ±0,0	0,4 ±0,0	0,1 ±0,0	0,2 ±0,0
	588/12	10,1 ±0,9	1,6 ±0,9	0,0 ±0,2	78,3 ±0,7	0,1 ±0,0	1,1 ±0,0	0,1 ±0,0	0,3 ±0,0	7,7 ±0,0	0,0 ±0,0	0,1 ±0,0	0,0 ±0,0	0,1 ±0,0	0,3 ±0,0	0,0 ±0,0	0,2 ±0,0
	588/14	11,2 ±0,9	1,9 ±0,9	0,0 ±0,2	80,2 ±0,8	0,0 ±0,0	0,8 ±0,0	0,1 ±0,0	0,2 ±0,0	5,3 ±0,0	0,0 ±0,0	0,2 ±0,0	0,0 ±0,0	0,2 ±0,0	0,1 ±0,0	0,0 ±0,0	0,0 ±0,0
	588/15	8,7 ±1,0	1,5 ±1,0	0,0 ±0,2	79,8 ±0,8	0,1 ±0,0	0,9 ±0,0	0,0 ±0,0	0,2 ±0,0	7,9 ±0,0	0,0 ±0,0	0,1 ±0,0	0,0 ±0,0	0,1 ±0,0	0,3 ±0,0	0,0 ±0,0	0,2 ±0,0
	588/16	11,0 ±1,0	1,4 ±1,0	0,0 ±0,2	77,6 ±0,7	0,1 ±0,0	1,0 ±0,0	0,1 ±0,0	0,2 ±0,0	7,8 ±0,0	0,0 ±0,0	0,1 ±0,0	0,0 ±0,0	0,1 ±0,0	0,3 ±0,0	0,0 ±0,0	0,2 ±0,0

Groups	Samples	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	Cl	K ₂ O	CaO	TiO ₂	MnO	Fe ₂ O ₃	As ₂ O ₃	PbO	BaO	Sb ₂ O ₅
	588/17	14,2	1,6 ±0,9	0,0 ±0,2	74,6 ±0,7	0,1 ±0,0	1,0 ±0,0	0,1 ±0,0	0,2 ±0,0	7,5 ±0,0	0,0 ±0,0	0,1 ±0,0	0,0 ±0,0	0,1 ±0,0	0,3 ±0,0	0,0 ±0,0	0,2 ±0,0
	588/18	10,6	1,6 ±0,9	0,0 ±0,2	78,3 ±0,7	0,1 ±0,0	0,7 ±0,0	0,0 ±0,0	0,2 ±0,0	7,6 ±0,0	0,0 ±0,0	0,1 ±0,0	0,0 ±0,0	0,1 ±0,0	0,3 ±0,0	0,0 ±0,0	0,2 ±0,0
	588/19	10,6	1,5 ±0,9	0,0 ±0,2	78,4 ±0,7	0,1 ±0,0	1,1 ±0,0	0,0 ±0,0	0,2 ±0,0	7,2 ±0,0	0,0 ±0,0	0,1 ±0,0	0,0 ±0,0	0,1 ±0,0	0,4 ±0,0	0,0 ±0,0	0,2 ±0,0
	588/20	9,1	1,7 ±1,0	0,0 ±0,2	79,2 ±0,8	0,1 ±0,0	0,9 ±0,0	0,1 ±0,0	0,3 ±0,0	7,8 ±0,0	0,0 ±0,0	0,1 ±0,0	0,0 ±0,0	0,1 ±0,0	0,4 ±0,0	0,0 ±0,0	0,2 ±0,0
	588/21	11,4	1,7 ±0,9	0,3 ±0,2	76,9 ±0,7	0,0 ±0,0	1,3 ±0,0	0,1 ±0,0	0,3 ±0,0	7,1 ±0,0	0,1 ±0,0	0,1 ±0,0	0,0 ±0,0	0,1 ±0,0	0,4 ±0,0	0,0 ±0,0	0,2 ±0,0
	588/23	13,6	1,6 ±0,9	0,0 ±0,2	75,6 ±0,7	0,1 ±0,0	0,6 ±0,0	0,0 ±0,0	0,2 ±0,0	7,4 ±0,0	0,0 ±0,0	0,1 ±0,0	0,0 ±0,0	0,1 ±0,0	0,3 ±0,0	0,0 ±0,0	0,2 ±0,0
	588/24	12,7	1,5 ±0,9	0,0 ±0,2	76,1 ±0,7	0,1 ±0,0	0,9 ±0,0	0,0 ±0,0	0,2 ±0,0	7,6 ±0,0	0,0 ±0,0	0,1 ±0,0	0,0 ±0,0	0,1 ±0,0	0,3 ±0,0	0,0 ±0,0	0,2 ±0,0
	588/25	12,7	1,4 ±0,9	0,0 ±0,2	78,4 ±0,7	0,0 ±0,0	1,1 ±0,0	0,1 ±0,0	0,1 ±0,0	5,7 ±0,0	0,0 ±0,0	0,2 ±0,0	0,1 ±0,0	0,2 ±0,0	0,1 ±0,0	0,0 ±0,0	0,0 ±0,0
	588/26	10,2	1,7 ±1,0	0,0 ±0,2	78,2 ±0,7	0,1 ±0,0	1,0 ±0,0	0,0 ±0,0	0,2 ±0,0	7,7 ±0,0	0,0 ±0,0	0,2 ±0,0	0,0 ±0,0	0,1 ±0,0	0,3 ±0,0	0,0 ±0,0	0,2 ±0,0
	588/27	12,2	1,5 ±0,9	0,0 ±0,2	76,5 ±0,7	0,1 ±0,0	1,3 ±0,0	0,0 ±0,0	0,3 ±0,0	7,2 ±0,0	0,0 ±0,0	0,1 ±0,0	0,0 ±0,0	0,2 ±0,0	0,4 ±0,0	0,0 ±0,0	0,2 ±0,0
	588/28	10,8	1,5 ±1,0	0,0 ±0,2	77,9 ±0,7	0,1 ±0,0	0,8 ±0,0	0,1 ±0,0	0,2 ±0,0	7,8 ±0,0	0,0 ±0,0	0,1 ±0,0	0,0 ±0,0	0,1 ±0,0	0,3 ±0,0	0,0 ±0,0	0,2 ±0,0
	588/29	10,0	1,5 ±0,9	0,0 ±0,2	78,7 ±0,8	0,0 ±0,0	1,0 ±0,0	0,1 ±0,0	0,2 ±0,0	7,7 ±0,0	0,0 ±0,0	0,1 ±0,0	0,0 ±0,0	0,1 ±0,0	0,3 ±0,0	0,0 ±0,0	0,2 ±0,0
	588/31	11,8	1,8 ±1,0	0,0 ±0,2	76,7 ±0,7	0,1 ±0,0	0,9 ±0,0	0,1 ±0,0	0,2 ±0,0	7,6 ±0,0	0,0 ±0,0	0,1 ±0,0	0,0 ±0,0	0,1 ±0,0	0,3 ±0,0	0,0 ±0,0	0,2 ±0,0
	588/32	14,8	1,9 ±0,9	0,0 ±0,2	73,8 ±0,7	0,1 ±0,0	1,0 ±0,0	0,1 ±0,0	0,2 ±0,0	7,4 ±0,0	0,0 ±0,0	0,1 ±0,0	0,0 ±0,0	0,1 ±0,0	0,3 ±0,0	0,0 ±0,0	0,2 ±0,0

Groups	Samples	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	Cl	K ₂ O	CaO	TiO ₂	MnO	Fe ₂ O ₃	As ₂ O ₃	PbO	BaO	Sb ₂ O ₅
	588/33	13,8	1,4 ±0,9	0,0 ±0,2	75,1 ±0,7	0,1 ±0,0	1,3 ±0,0	0,0 ±0,0	0,3 ±0,0	7,1 ±0,0	0,0 ±0,0	0,1 ±0,0	0,0 ±0,0	0,2 ±0,0	0,4 ±0,0	0,0 ±0,0	0,2 ±0,0
	588/36	16,9	1,7 ±0,9	0,0 ±0,2	73,6 ±0,7	0,0 ±0,0	1,5 ±0,0	0,0 ±0,0	0,1 ±0,0	5,5 ±0,0	0,0 ±0,0	0,2 ±0,0	0,0 ±0,0	0,2 ±0,0	0,3 ±0,0	0,0 ±0,0	0,0 ±0,0
	588/38	11,2	1,5 ±0,9	0,0 ±0,2	77,6 ±0,7	0,1 ±0,0	1,5 ±0,0	0,0 ±0,0	0,2 ±0,0	6,8 ±0,0	0,0 ±0,0	0,1 ±0,0	0,0 ±0,0	0,2 ±0,0	0,4 ±0,0	0,0 ±0,0	0,2 ±0,0
	588/39	10,5	1,8 ±0,9	0,0 ±0,2	77,9 ±0,7	0,1 ±0,0	0,9 ±0,0	0,1 ±0,0	0,2 ±0,0	7,7 ±0,0	0,0 ±0,0	0,2 ±0,0	0,0 ±0,0	0,1 ±0,0	0,3 ±0,0	0,0 ±0,0	0,2 ±0,0
	588/40	10,5	1,5 ±0,9	0,0 ±0,2	78,1 ±0,7	0,1 ±0,0	0,9 ±0,0	0,0 ±0,0	0,2 ±0,0	7,7 ±0,0	0,0 ±0,0	0,1 ±0,0	0,0 ±0,0	0,1 ±0,0	0,3 ±0,0	0,0 ±0,0	0,2 ±0,0
	588/41	10,4	1,7 ±0,9	0,0 ±0,2	78,3 ±0,7	0,1 ±0,0	0,7 ±0,0	0,1 ±0,0	0,2 ±0,0	7,8 ±0,0	0,0 ±0,0	0,1 ±0,0	0,0 ±0,0	0,1 ±0,0	0,3 ±0,0	0,0 ±0,0	0,2 ±0,0
	588/42	10,2	1,7 ±0,9	0,0 ±0,2	78,5 ±0,7	0,1 ±0,0	0,7 ±0,0	0,1 ±0,0	0,2 ±0,0	7,7 ±0,0	0,0 ±0,0	0,2 ±0,0	0,0 ±0,0	0,1 ±0,0	0,3 ±0,0	0,0 ±0,0	0,2 ±0,0
	588/43	12,3	1,6 ±1,0	0,0 ±0,2	76,4 ±0,7	0,1 ±0,0	1,0 ±0,0	0,1 ±0,0	0,2 ±0,0	7,6 ±0,0	0,0 ±0,0	0,1 ±0,0	0,0 ±0,0	0,1 ±0,0	0,3 ±0,0	0,0 ±0,0	0,2 ±0,0
	588/44	12,4	1,2 ±0,9	0,0 ±0,2	76,8 ±0,7	0,1 ±0,0	1,2 ±0,0	0,0 ±0,0	0,2 ±0,0	7,2 ±0,0	0,0 ±0,0	0,1 ±0,0	0,0 ±0,0	0,1 ±0,0	0,4 ±0,0	0,0 ±0,0	0,2 ±0,0
	588/45	15,6	1,4 ±0,9	0,0 ±0,2	73,0 ±0,7	0,1 ±0,0	1,5 ±0,0	0,0 ±0,0	0,3 ±0,0	7,1 ±0,0	0,0 ±0,0	0,1 ±0,0	0,1 ±0,0	0,1 ±0,0	0,4 ±0,0	0,0 ±0,0	0,2 ±0,0
	588/46	12,8	1,4 ±0,9	0,0 ±0,2	76,3 ±0,7	0,1 ±0,0	0,7 ±0,0	0,1 ±0,0	0,2 ±0,0	7,6 ±0,0	0,0 ±0,0	0,1 ±0,0	0,0 ±0,0	0,1 ±0,0	0,3 ±0,0	0,0 ±0,0	0,2 ±0,0
	588/47	14,8	1,7 ±1,0	0,0 ±0,2	74,0 ±0,7	0,1 ±0,0	0,8 ±0,0	0,1 ±0,0	0,2 ±0,0	7,5 ±0,0	0,0 ±0,0	0,1 ±0,0	0,0 ±0,0	0,1 ±0,0	0,3 ±0,0	0,0 ±0,0	0,2 ±0,0
	588/49	11,5	1,5 ±1,0	0,0 ±0,2	77,4 ±0,7	0,1 ±0,0	0,7 ±0,0	0,1 ±0,0	0,3 ±0,0	7,7 ±0,0	0,0 ±0,0	0,1 ±0,0	0,0 ±0,0	0,1 ±0,0	0,3 ±0,0	0,0 ±0,0	0,2 ±0,0
	588/50	12,6	1,3 ±0,9	0,0 ±0,2	76,4 ±0,7	0,1 ±0,0	1,1 ±0,0	0,1 ±0,0	0,2 ±0,0	7,3 ±0,0	0,1 ±0,0	0,1 ±0,0	0,0 ±0,0	0,1 ±0,0	0,4 ±0,0	0,0 ±0,0	0,2 ±0,0

Groups	Samples	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	Cl	K ₂ O	CaO	TiO ₂	MnO	Fe ₂ O ₃	As ₂ O ₃	PbO	BaO	Sb ₂ O ₅
	588/51	10,6	1,7 ±0,9	0,0 ±0,2	77,9 ±0,7	0,1 ±0,0	0,9 ±0,0	0,0 ±0,0	0,3 ±0,0	7,7 ±0,0	0,0 ±0,0	0,2 ±0,0	0,0 ±0,0	0,1 ±0,0	0,3 ±0,0	0,0 ±0,0	0,2 ±0,0
	588/52	12,6	1,6 ±0,9	0,0 ±0,2	75,7 ±0,7	0,1 ±0,0	1,2 ±0,0	0,1 ±0,0	0,3 ±0,0	7,6 ±0,0	0,0 ±0,0	0,1 ±0,0	0,0 ±0,0	0,1 ±0,0	0,3 ±0,0	0,0 ±0,0	0,2 ±0,0
	588/53	16,6	1,8 ±0,9	0,0 ±0,2	73,0 ±0,7	0,0 ±0,0	1,4 ±0,0	0,0 ±0,0	0,2 ±0,0	6,6 ±0,0	0,0 ±0,0	0,1 ±0,0	0,0 ±0,0	0,2 ±0,0	0,4 ±0,0	0,0 ±0,0	0,2 ±0,0
	588/54	12,8	1,7 ±0,9	0,0 ±0,2	76,1 ±0,7	0,1 ±0,0	0,7 ±0,0	0,0 ±0,0	0,2 ±0,0	7,6 ±0,0	0,0 ±0,0	0,1 ±0,0	0,1 ±0,0	0,1 ±0,0	0,3 ±0,0	0,0 ±0,0	0,2 ±0,0
	588/55	13,9	1,7 ±1,0	0,0 ±0,2	74,6 ±0,7	0,1 ±0,0	1,1 ±0,0	0,0 ±0,0	0,2 ±0,0	7,6 ±0,0	0,0 ±0,0	0,1 ±0,0	0,0 ±0,0	0,1 ±0,0	0,3 ±0,0	0,0 ±0,0	0,2 ±0,0
	588/56	11,2	1,6 ±0,9	0,0 ±0,2	77,8 ±0,7	0,01 ±0,0	0,6 ±0,0	0,1 ±0,0	0,2 ±0,0	7,7 ±0,0	0,0 ±0,0	0,1 ±0,0	0,0 ±0,0	0,1 ±0,0	0,3 ±0,0	0,0 ±0,0	0,2 ±0,0
	588/59	14,0	1,2 ±0,9	0,1 ±0,2	75,5 ±0,7	0,0 ±0,0	1,6 ±0,0	0,0 ±0,0	0,3 ±0,0	6,0 ±0,0	0,0 ±0,0	0,2 ±0,0	0,0 ±0,0	0,3 ±0,0	0,6 ±0,0	0,0 ±0,0	0,0 ±0,0
	588/60	11,7	2,0 ±1,0	0,0 ±0,2	78,1 ±0,7	0,1 ±0,0	0,8 ±0,0	0,1 ±0,0	0,2 ±0,0	6,2 ±0,0	0,0 ±0,0	0,2 ±0,0	0,1 ±0,0	0,2 ±0,0	0,2 ±0,0	0,0 ±0,0	0,0 ±0,0
	588/61	16,6	1,2 ±0,9	0,0 ±0,2	74,0 ±0,7	0,0 ±0,0	2,0 ±0,0	0,0 ±0,0	0,2 ±0,0	5,0 ±0,0	0,0 ±0,0	0,2 ±0,0	0,0 ±0,0	0,3 ±0,0	0,4 ±0,0	0,1 ±0,0	0,0 ±0,0
	588/62	17,8	1,3 ±0,9	0,00 ±0,2	72,5 ±0,7	0,1 ±0,0	1,9 ±0,0	0,0 ±0,0	0,1 ±0,0	5,6 ±0,0	0,0 ±0,0	0,2 ±0,0	0,0 ±0,0	0,2 ±0,0	0,2 ±0,0	0,0 ±0,0	0,0 ±0,0
	588/64	13,9	1,9 ±0,9	0,0 ±0,2	76,5 ±0,7	0,1 ±0,0	0,9 ±0,0	0,1 ±0,0	0,1 ±0,0	5,9 ±0,0	0,0 ±0,0	0,2 ±0,0	0,0 ±0,0	0,2 ±0,0	0,2 ±0,0	0,0 ±0,0	0,0 ±0,0
	588/65	14,9	1,7 ±0,9	0,0 ±0,2	74,3 ±0,7	0,1 ±0,0	0,9 ±0,0	0,0 ±0,0	0,3 ±0,0	6,4 ±0,0	0,0 ±0,0	0,2 ±0,0	0,1 ±0,0	0,2 ±0,0	0,8 ±0,0	0,0 ±0,0	0,0 ±0,0
	588/66	11,5	1,6 ±0,9	0,0 ±0,2	77,3 ±0,7	0,1 ±0,0	1,0 ±0,0	0,1 ±0,0	0,3 ±0,0	6,8 ±0,0	0,0 ±0,0	0,2 ±0,0	0,1 ±0,0	0,2 ±0,0	0,6 ±0,0	0,0 ±0,0	0,2 ±0,0
	588/67	12,3	1,2 ±0,8	0,1 ±0,2	77,6 ±0,7	0,0 ±0,0	1,9 ±0,0	0,0 ±0,0	0,2 ±0,0	5,4 ±0,0	0,0 ±0,0	0,2 ±0,0	0,0 ±0,0	0,2 ±0,0	0,7 ±0,0	0,0 ±0,0	0,0 ±0,0

Groups	Samples	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	Cl	K ₂ O	CaO	TiO ₂	MnO	Fe ₂ O ₃	As ₂ O ₃	PbO	BaO	Sb ₂ O ₅	
2	588/68	10,8	1,6 ±1,0	0,1 ±0,2	76,9 ±0,7	0,1 ±0,0	1,8 ±0,0	0,1 ±0,0	0,4 ±0,0	6,7 ±0,0	0,0 ±0,0	0,2 ±0,0	0,1 ±0,0	0,2 ±0,0	0,8 ±0,0	0,0 ±0,0	0,0 ±0,0	
	588/69	11,9	1,9 ±1,0	0,0 ±0,0	77,1 ±0,7	0,1 ±0,0	0,8 ±0,0	0,1 ±0,0	0,3 ±0,0	6,8 ±0,0	0,0 ±0,0	0,2 ±0,0	0,1 ±0,0	0,2 ±0,0	0,7 ±0,0	0,0 ±0,0	0,0 ±0,0	
	588/70	22,8	0,5 ±0,8	0,1 ±0,2	68,4 ±0,6	0,0 ±0,0	2,0 ±0,0	0,0 ±0,0	0,2 ±0,0	5,1 ±0,0	0,0 ±0,0	0,2 ±0,0	0,0 ±0,0	0,2 ±0,0	0,3 ±0,0	0,0 ±0,0	0,1 ±0,0	
	588/71	11,5	1,0 ±0,8	0,1 ±0,2	77,9 ±0,7	0,0 ±0,0	1,9 ±0,0	0,0 ±0,0	0,4 ±0,0	5,7 ±0,0	0,0 ±0,0	0,2 ±0,0	0,0 ±0,0	0,2 ±0,0	0,9 ±0,0	0,0 ±0,0	0,0 ±0,0	
	588/72	12,4	1,4 ±0,9	0,1 ±0,2	77,8 ±0,7	0,0 ±0,0	1,9 ±0,0	0,1 ±0,0	0,2 ±0,0	6,0 ±0,0	0,0 ±0,0	0,1 ±0,0	0,0 ±0,0	0,1 ±0,0	0,2 ±0,0	0,0 ±0,0	0,0 ±0,0	
	588/73	14,1	0,9 ±0,9	0,1 ±0,2	76,5 ±0,7	0,0 ±0,0	2,0 ±0,0	0,0 ±0,0	0,2 ±0,0	5,4 ±0,0	0,0 ±0,0	0,2 ±0,0	0,0 ±0,0	0,2 ±0,0	0,3 ±0,0	0,1 ±0,0	0,0 ±0,0	
	588/74	13,9	1,9 ±0,9	0,9 ±0,3	75,4 ±0,7	0,0 ±0,0	0,9 ±0,0	0,1 ±0,0	1,3 ±0,0	5,4 ±0,0	0,0 ±0,0	0,0 ±0,0	0,1 ±0,0	0,0 ±0,0	0,0 ±0,0	0,0 ±0,0	0,0 ±0,0	
	588/7	10,5	0,8 ±0,9	0,0 ±0,2	75,8 ±0,7	0,1 ±0,0	0,7 ±0,0	0,2 ±0,0	3,7 ±0,0	7,5 ±0,0	0,0 ±0,0	0,1 ±0,0	0,0 ±0,0	0,2 ±0,0	0,0 ±0,0	0,0 ±0,0	0,0 ±0,0	0,4 ±0,0
	588/11	20,4	0,7 ±0,9	0,5 ±0,3	66,0 ±0,6	0,0 ±0,0	1,5 ±0,0	0,2 ±0,0	3,3 ±0,0	6,6 ±0,0	0,0 ±0,0	0,1 ±0,0	0,0 ±0,0	0,3 ±0,0	0,0 ±0,0	0,0 ±0,0	0,0 ±0,0	0,4 ±0,0
	588/13	11,7	0,5 ±0,9	0,3 ±0,2	75,1 ±0,7	0,1 ±0,0	1,2 ±0,0	0,1 ±0,0	3,7 ±0,0	6,5 ±0,0	0,0 ±0,0	0,1 ±0,0	0,0 ±0,0	0,3 ±0,0	0,0 ±0,0	0,0 ±0,0	0,0 ±0,0	0,4 ±0,0
	588/22	11,4	0,7 ±0,9	0,3 ±0,3	74,6 ±0,7	0,1 ±0,0	0,8 ±0,0	0,2 ±0,0	3,8 ±0,0	7,1 ±0,0	0,0 ±0,0	0,1 ±0,0	0,0 ±0,0	0,2 ±0,0	0,0 ±0,0	0,0 ±0,0	0,0 ±0,0	0,4 ±0,0
	588/30	12,6	0,6 ±0,9	0,3 ±0,2	73,7 ±0,7	0,1 ±0,0	1,0 ±0,0	0,3 ±0,0	3,6 ±0,0	7,0 ±0,0	0,0 ±0,0	0,1 ±0,0	0,1 ±0,0	0,2 ±0,0	0,0 ±0,0	0,0 ±0,0	0,0 ±0,0	0,4 ±0,0
	588/34	13,7	0,7 ±0,9	0,5 ±0,2	72,7 ±0,7	0,1 ±0,0	1,3 ±0,0	0,1 ±0,0	3,6 ±0,0	6,5 ±0,0	0,0 ±0,0	0,1 ±0,0	0,0 ±0,0	0,3 ±0,0	0,0 ±0,0	0,0 ±0,0	0,0 ±0,0	0,4 ±0,0
	588/35	15,0	0,8 ±0,8	0,8 ±0,2	70,9 ±0,7	0,1 ±0,0	1,1 ±0,0	0,3 ±0,0	3,5 ±0,0	6,8 ±0,0	0,0 ±0,0	0,1 ±0,0	0,0 ±0,0	0,2 ±0,0	0,0 ±0,0	0,0 ±0,0	0,0 ±0,0	0,4 ±0,0

Groups	Samples	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	Cl	K ₂ O	CaO	TiO ₂	MnO	Fe ₂ O ₃	As ₂ O ₃	PbO	BaO	Sb ₂ O ₅
	588/37	12,5	0,9 ±0,9	0,4 ±0,2	73,0 ±0,7	0,1 ±0,0	1,2 ±0,0	0,3 ±0,0	3,9 ±0,0	6,8 ±0,0	0,0 ±0,0	0,1 ±0,0	0,0 ±0,0	0,3 ±0,0	0,0 ±0,0	0,0 ±0,0	0,4 ±0,0
	588/57	12,7	0,6 ±0,9	0,2 ±0,2	73,8 ±0,7	0,1 ±0,0	0,9 ±0,0	0,2 ±0,0	3,7 ±0,0	6,9 ±0,0	0,0 ±0,0	0,1 ±0,0	0,0 ±0,0	0,3 ±0,0	0,0 ±0,0	0,0 ±0,0	0,4 ±0,0
	588/58	7,9	0,9 ±0,9	0,0 ±0,2	78,9 ±0,8	0,0 ±0,0	0,2 ±0,0	0,0 ±0,0	7,2 ±0,1	4,3 ±0,0	0,0 ±0,0	0,0 ±0,0	0,0 ±0,0	0,0 ±0,0	0,0 ±0,0	0,4 ±0,0	0,0 ±0,0
	588/63	6,0	1,4 ±0,9	0,0 ±0,2	79,9 ±0,8	0,1 ±0,0	1,0 ±0,0	0,1 ±0,0	4,6 ±0,0	6,4 ±0,0	0,0 ±0,0	0,2 ±0,0	0,1 ±0,0	0,2 ±0,0	0,2 ±0,0	0,0 ±0,0	0,0 ±0,0
Outlier	588/48	43,4	1,5 ±0,9	0,0 ±0,2	48,5 ±0,6	0,0 ±0,0	0,5 ±0,0	0,1 ±0,0	1,2 ±0,0	4,0 ±0,0	0,0 ±0,0	0,1 ±0,0	0,0 ±0,0	0,1 ±0,0	0,3 ±0,0	0,0 ±0,0	0,2 ±0,0

Table VI.2. p-XRF values obtained for the glass standards, with the calculation of relative accuracy (in percentage), based on the certified standard values^[1]. p-XRF and certified standard values are presented in weight percent (wt%). Na₂O values are obtained through the sum of all components, including residuals, minus 100.

Standards	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	K ₂ O	CaO	TiO ₂	MnO	Fe ₂ O ₃	PbO	BaO	Sb ₂ O ₅
Corning A (CMoG A)													
p-XRF	12,8	3,2 ±1,1	0,3 ±0,3	69,8 ±0,7	0,1 ±0,0	2,7 ±0,0	5,2 ±0,0	0,9 ±0,0	1,1 ±0,0	1,0 ±0,0	0,1 ±0,0	0,1 ±0,0	1,3 ±0,0
Certified	14,30	2,66	1,00	67,03	0,13	2,87	5,03	0,79	1,00	1,09	0,12	0,56	1,75
Rel. Acc.	10,38	19,89	69,50	4,17	40,01	7,21	2,41	9,68	11,10	4,72	56,90	75,88	24,57
Corning B (CMoG B)													
p-XRF	7,4	1,6 ±1,0	4,4 ±0,4	69,9 ±0,7	0,8 ±0,0	1,0 ±0,0	8,9 ±0,0	0,1 ±0,0	0,3 ±0,0	0,4 ±0,0	0,5 ±0,0	0,1 ±0,0	0,5 ±0,0
Certified	17,00	1,03	4,36	62,27	0,82	1,00	8,56	0,09	0,25	0,34	0,61	0,12	0,46
Rel. Acc.	56,64	51,17	1,10	12,25	1,54	2,90	3,41	39,97	6,32	7,56	18,03	59,08	1,33

References:

- [1] Brill, R. H. 1999. *Chemical Analyses of Early Glasses*, vol. 2, The Tables. Corning, New York: The Corning Museum of Glass.

Appendix VII. ICP-AES and HPIC: Selection criteria, sample collection and analytical results

a) Selection criteria for sampling

1. Each chemical stored inside the portable set of chemicals in study was evaluated according safety information found in MSDS for the respective modern chemical and according to the restrictions implemented by the regulatory entities - European Unions' Agency for Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) and the United States of America's Occupational Safety and Health Administration (OSHA) -, on hazardous materials. As a result, for the sampling purposes, **all chemicals identified as a risk of acute toxicity or carcinogenic were excluded from sampling.**
2. **pH value** of a chemical based on theoretical values, through comparison with the modern manufacture of the same compound, associating with the **damage observed to the glass**, based on macroscopic observation of the corrosion found in the glass containers.
 - 2.1. Preferably chemicals with theoretical values in the extremes of the pH scale;
 - 2.2. Chemical's with a theoretical pH in which glass deterioration is not expected, but corrosion patterns are identified. These may be selected for sampling, under the assumption that the chemical has had its properties sufficiently altered so the glasses become damaged.
3. **Possibility of unsealing the stoppers.** All the chemicals in the case-study object have been sealed on the stoppers due to safety measures, to prevent off-gassing from the chemicals. It has been found that some were sealed with paraffin, therefore, making the unsealing process possible. However, some containers appear to have been sealed with a harder unidentified material, making the unsealing process impossible without the action of harsh solvents which may compromise the chemical stored inside in the removal process, or the glass itself.

b) Sample collection protocol

To unseal the selected containers (Figures VIII. 1 and VIII.2) and collect the samples for analysis, the following steps were taken:

1. Wet cleaning with distilled water on the sealing area of the stopper.
2. Slowly try to rotate the stopper to attempt to soften the sealant – in case of paraffin, it was at times weakened enough to allow for the rotation and opening of the container.
3. In the case of a more hardened sealant, small cotton rolls dampened with hot water (heated to 60°-70°C) were applied to the sealed region, to soften the sealant. This step was repeated until rotation of the stopper was achieved.
4. After the opening of the chemicals, 1ml of solution was sampled directly from the inside of the glass container, with a graduated pipette and a pump, and stored into plastic containers appropriate for sample storage for analysis.
5. pH of the collected solutions was measured. Each solution was measured 3 times and an average was calculated. Table VIII.I compiles all the obtained values and the average.



Figure VII.1. Selected chemicals for sampling. From left to right: Zinc sulphate; Strontium chloride; Sodium sulphate; Calcium chloride; Manganese chloride.



Figure VII.2. Selected chemicals for sampling. From left to right: Magnesium sulphate; Sodium phosphate; Magnesium mixture; Lithium chloride

Table VII.1. pH measurements of all the collected samples and calculated average.

Sample	Measurement 1	Measurement 2	Measurement 3	Average
Zinc sulphate (UL000588/2)	5,58	5,50	5,39	5,49
Strontium chloride (UL000588/12)	7,73	7,84	7,83	7,80
Sodium sulphate (UL000588/16)	1,59	1,62	1,63	1,61
Calcium chloride (UL000588/20)	6,97	6,98	7,05	7,00
Manganese chloride (UL000588/25)	5,43	5,78	5,75	5,65
Magnesium sulphate (UL000588/35)	6,88	7,11	6,60	6,86
Sodium phosphate (UL000588/51)	8,82	8,87	8,83	8,84
Magnesium mixture (UL000588/64)	9,35	9,37	9,35	9,40
Lithium chloride (UL000588/65)	8,00	8,01	7,98	8,00

c) ICP-AES and HPIC results**Table VII.2.** ICP-AES and HPIC results for all samples. Values are expressed in milligrams per litre (mg/L) or ppm.

Sample	ICP-AES		HPIC	
	Elements	Concentration	Ionic species	Concentration
Zinc sulphate (UL000588/2)	Zn	19977	SO ₄ ²⁻	31646,8
	S	9505	Cl ⁻	1239,3
Strontium chloride (UL000588/12)	Sr	10440	Cl ⁻	29927,2
Sodium sulphate (UL000588/16)	Na	7702	SO ₄ ²⁻	32423,4
	S	10390	Cl ⁻	892,8
Calcium chloride (UL000588/20)	Ca	56749	Cl ⁻	102187,9
Manganese chloride (UL000588/25)	Mn	29078	Cl ⁻	36021,7
Magnesium sulphate (UL000588/35)	Mg	18771	SO ₄ ²⁻	73765,2
	S	25378	Cl ⁻	912,6
Sodium phosphate (UL000588/51)	Na	6216	PO ₄ ³⁻	29044,0
	P	59,04	Cl ⁻	795,4
Magnesium mixture (UL000588/64)	Mg	1436	----	
	Ca	14,71		
Lithium chloride (UL000588/65)	Li	7752	Cl ⁻	33599,2

Appendix VIII. Survey to institutions holding collections of historical chemicals

a) Survey summary:

Table VIII.1 Table compiling the summary of responses from the survey.

Composition of collections	Display/storage conditions	Glass containers deterioration
<ul style="list-style-type: none">Collection sizes vary;Mostly dating from the 19th and 20th centuries;Mostly associated to the areas of chemistry, medicine or pigments/dyes;Mostly kept in glass containers;Chemicals are still present within the containers;	<ul style="list-style-type: none">Storage and display materials vary from wood, metal or glass;Chemicals are mostly displayed according to historical significance;	<ul style="list-style-type: none">Deterioration is found most commonly under the form of loss of transparency, formation of products or iridescent layers;Damages are most prevalent on the insides of the containers;
Safety & Conservation measures	Optional questions	
<ul style="list-style-type: none">Toxic chemicals are mostly present in the collections;The majority of institutions take preventive conservation measures;Most common measures adopted by the institutions are: environmental control, inventory and documentation, light control and monitoring for materials alterations;	<ul style="list-style-type: none">Label deterioration;Alteration of the chemicals;	

b) Survey body and responses

CONSERVATION PRACTICES IN HISTORICAL COLLECTIONS OF CHEMICALS

Welcome!

In the context of a master's dissertation in Conservation and Restoration, from the NOVA University of Lisbon, a study is undergoing to evaluate the deterioration of glass containers in the historical collection of chemicals from the National Museum of Natural History and Science of the University of Lisbon (MUHNAC). As part of this dissertation, the present survey aims to gather information regarding conservation practices, at an international scale, to collections that contain historical chemicals – this is, chemical substances exhibited and/or preserved as material culture, at museums or institutional contexts.

This survey has two main purposes:

- To understand, in regard to chemicals stored inside glass containers, the corrosion patterns that may be exhibited in the glass material, and if there is a connection with the nature of the chemical substances within the containers.
- To aid in the construction of conservation guidelines for this type of collections: these intend to overview internal and external factors that may compromise the preservation of

such objects. As such, it is imperative to understand how these collections exist within other museums or institutions and what their conservation practices are.

The survey should take about 10 to 15 minutes to complete.

Confidentiality disclaimer: All the data gathered from this survey will only be used for the purposes of dissertation related work. Only the participating institutions' names will be presented, and all the responses will be anonymised and presented statistically in published materials.

For more information or questions regarding the work in development, please feel free to contact at ar.lourenco@campus.fct.unl.pt.

(This survey was open from January to August 2019, on the platform GoogleForms)

PARTICIPATING INSTITUTIONS

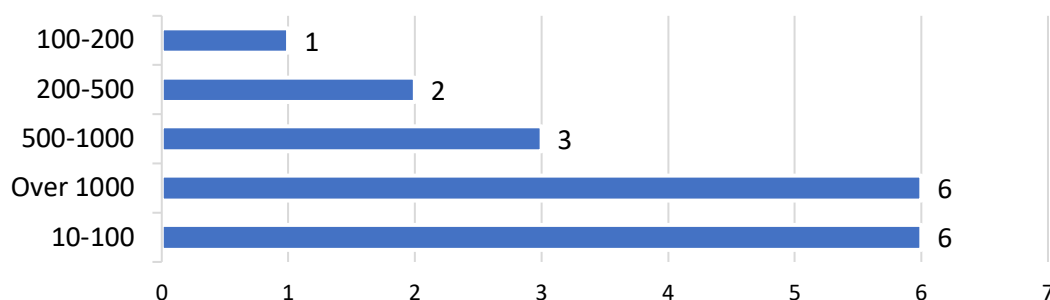
Europe	North America
Saúde Museum (Portugal)	Allen King Collection of Scientific Instruments - Dartmouth College (United States of America)
Pharmacy Museum (Portugal)	
Science Museum of the University of Coimbra (Portugal)	
Museum of Natural History and Science of the University of Porto (Portugal)	The Mütter Museum of the College of Physicians of Philadelphia (United States of America)
Collection of the Department of Pharmacology - University of Granada (Spain)	
Museum of the Hispanic Pharmacy – Universidad Complutense de Madrid (Spain)	Robert A. Paselk Scientific Instrument Museum – Humboldt State University (United States of America)
Old Scientific Laboratory of Natural, Physical and Chemistry Sciences – Università Degli Studi Suor Orsola Benincasa (Italy)	
Whipple Museum of the History of Science (United Kingdom)	Forbes Pigment Collection - Harvard Art Museums (United States of America)
Chemistry Collection – University of Dundee (United Kingdom)	
Hans Fischer Chemicals Collection – Technical University of Munich (Germany)	
Collection of Inorganic-Chemical Preparations - TU Bergakademie Freiberg (Germany)	
Ghent University Museum (Belgium)	
Rijksmuseum Boerhaave (Netherlands)	
Chemical and Pharmacognostical Collection – ETH Zurich (Switzerland)	
Norwegian University of Science and Technology (Norway)	
The Great Serbian Chemists' Collection – University of Belgrade (Serbia)	

Oceania
School of Chemistry Collection – University of Melbourne (Australia)

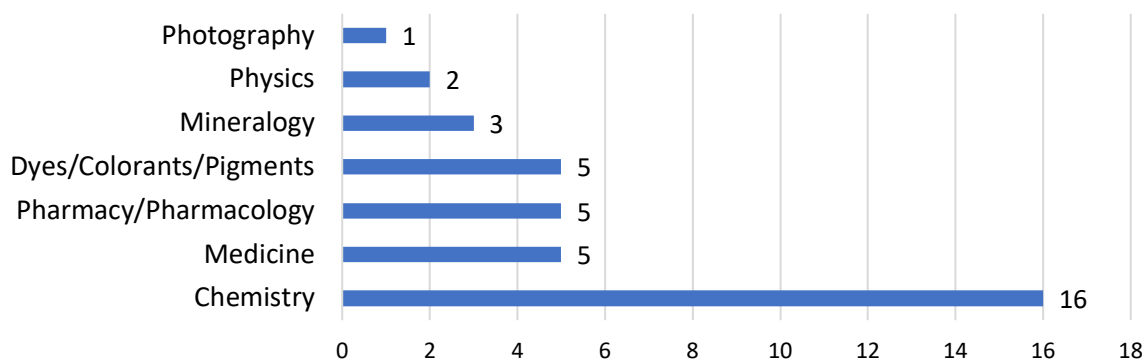
SECTION 1 – THE COLLECTION

This section aims to understand how collections are composed in terms of dimension, disciplinary areas, date and typology.

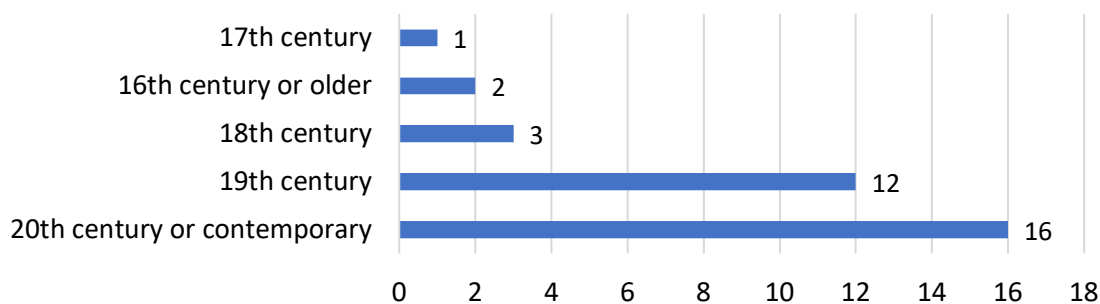
1.1. Is there an estimate number of how many chemicals are currently present in your collection?



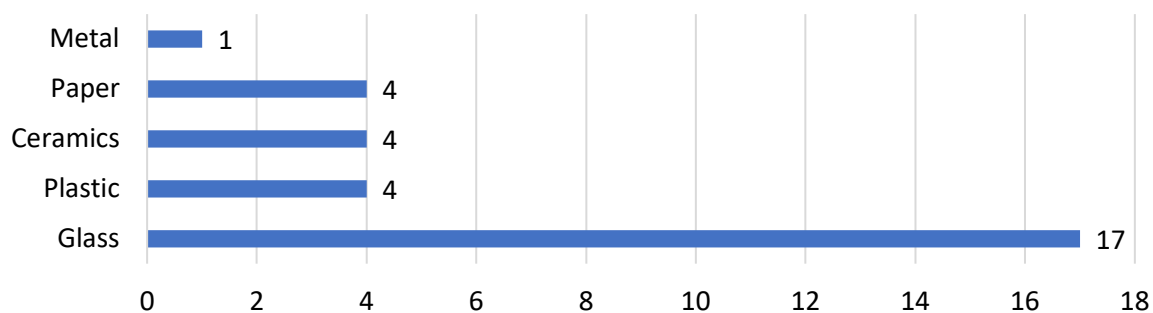
1.2. The context of use of the chemicals present in your collection come from which field(s)?



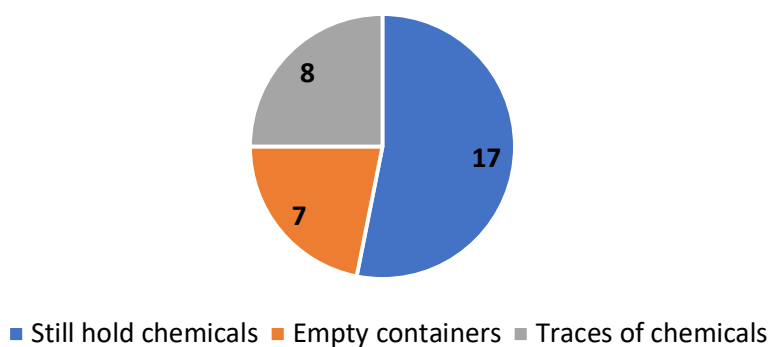
1.3. Is there a specific period(s) in which your collection inserts?



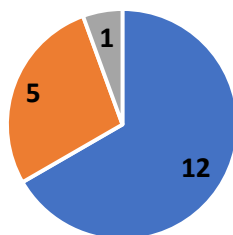
1.4. What material are the containers your chemicals are kept in?



1.5. Do the containers in your collection still hold chemicals inside?



1.6. Do the chemicals in your collection appear to have been used?

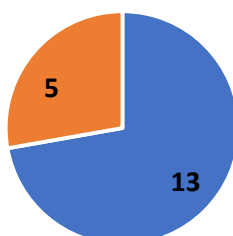


■ Some used, others unopened ■ Yes ■ No

SECTION 2 – EXHIBITION & STORAGE

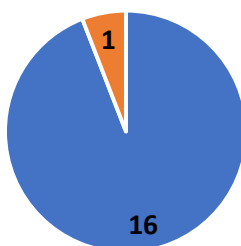
This section aims to understand how the collections are exhibited or stored.

2.1. Do you currently have any chemicals in permanent or temporary exhibition?



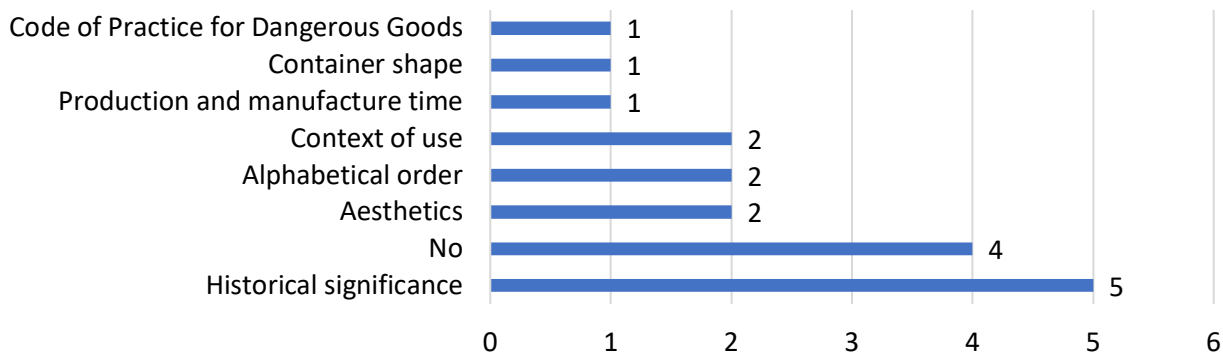
■ Yes ■ No

2.2. Do you currently have any chemicals in storage?

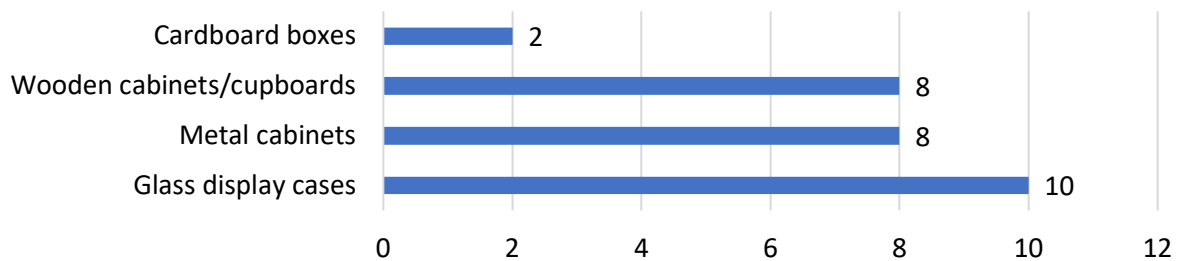


■ Yes ■ No

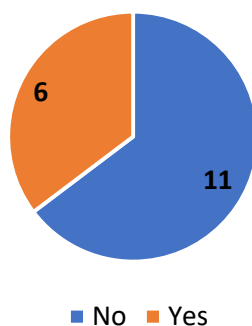
2.3. For chemicals currently in storage or display, is there any criteria for their selection (e.g. dichotomic organization, historical significance or by context of use)?



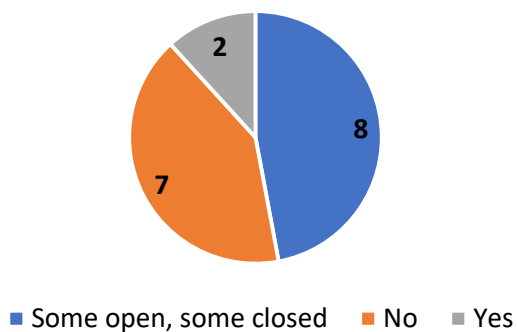
2.4. How are these chemicals stored (either in dedicated storage and/or exhibition)?



2.5. Are the exhibition/storage materials also historical or associated with the collection (e.g. original cabinets where the collection has always been stored in)?



2.6. Are the cabinets/display cases open?

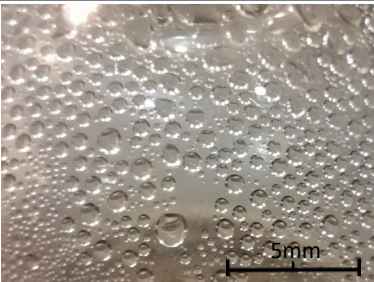
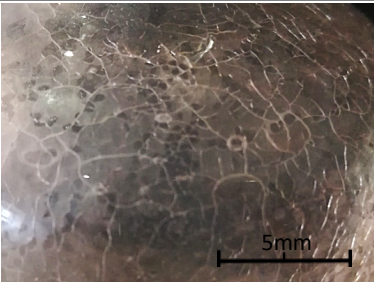
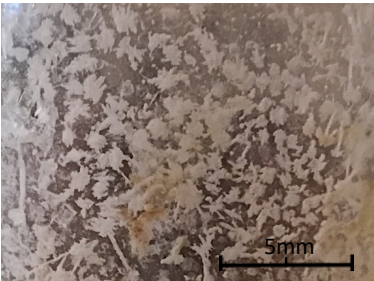
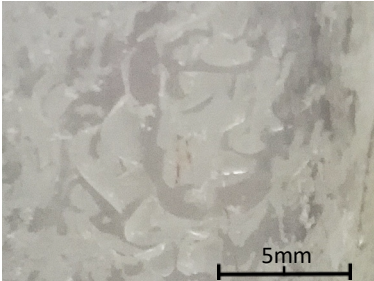
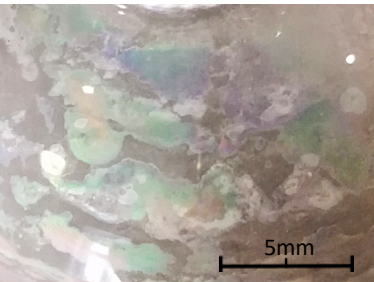
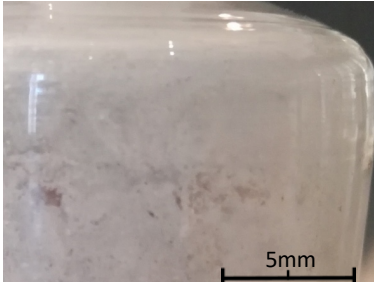
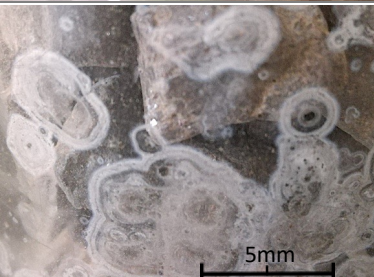



SECTION 3 – GLASS CONTAINERS

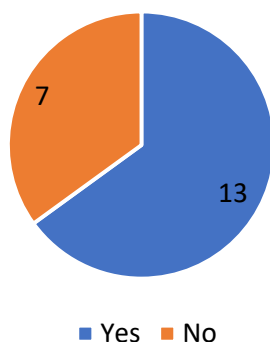
In this section, the goal is to understand the corrosion of the glass containers in collections.

If your collection does not present chemicals stored inside glass containers, please skip this section.

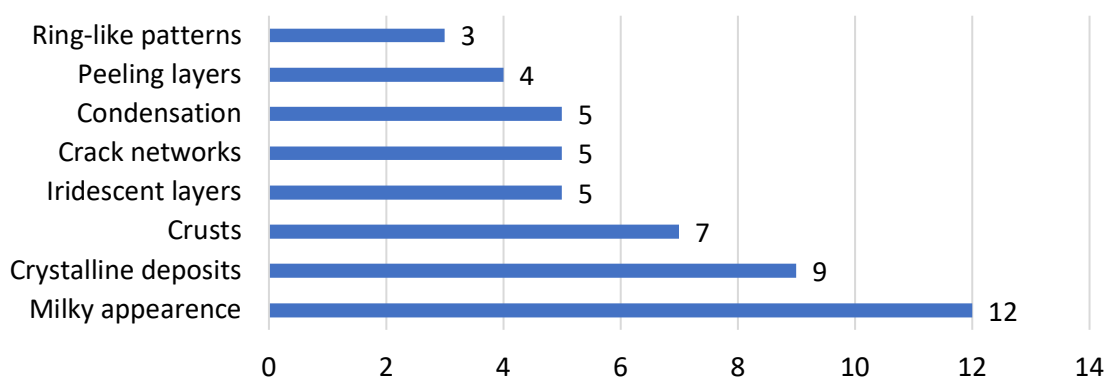
The following table presents some of the most prevalent patterns associated to the corrosion of glass, found in the chemicals' containers from the MUHNAC-UL collection.

	Damage observed		Damage observed
Condensation		Crack networks	
Crystalline deposits on the glass surface		Peeling layers	
Iridescent layers		Milky appearance	
Ring-like patterns		Crusts	

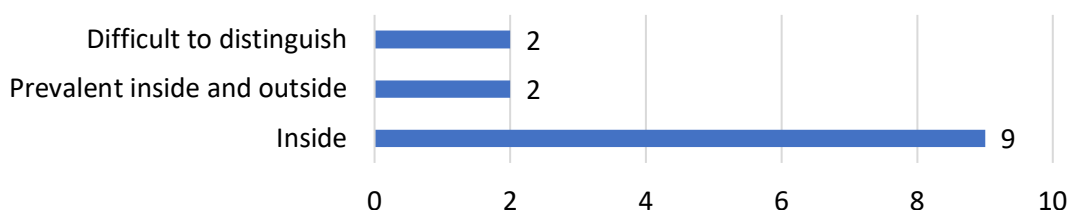
3.1. Taking into consideration the table previously shown, do your collection’s glass containers present any similar damages?



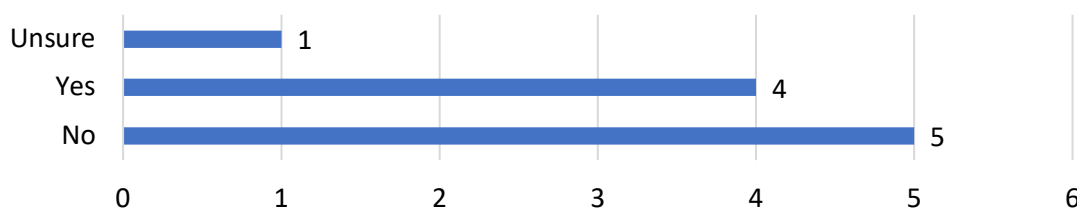
3.2. If you answered “Yes” in the previous question, please select which damages you identify in your own collection:



3.3. Would you consider that the damages are most prevalent on the inside of the container or on the outside?



3.4. In your opinion, is there a relation between the chemical stored inside the container and the corrosion observed? For example, alkaline compounds showing more signs of corrosion than acidic compounds or vice-versa.

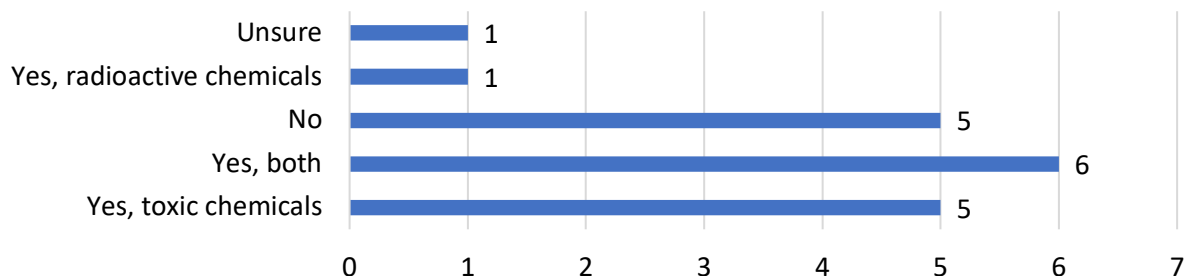


SECTION 4 – SAFETY & CONSERVATION PRACTICES

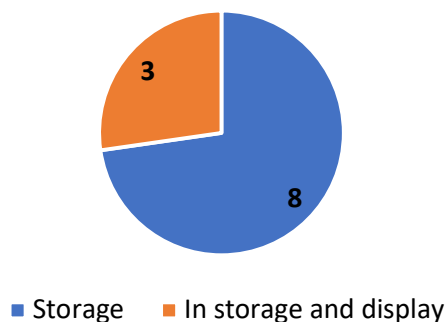
This section aims to understand which safety and conservation measures are taken.

4.1. Regarding known toxic chemicals, that could normally exist in these type of collections (e.g. arsenic, cyanides or mercury compounds) and radioactive chemicals (e.g. thorium or uranium compounds):

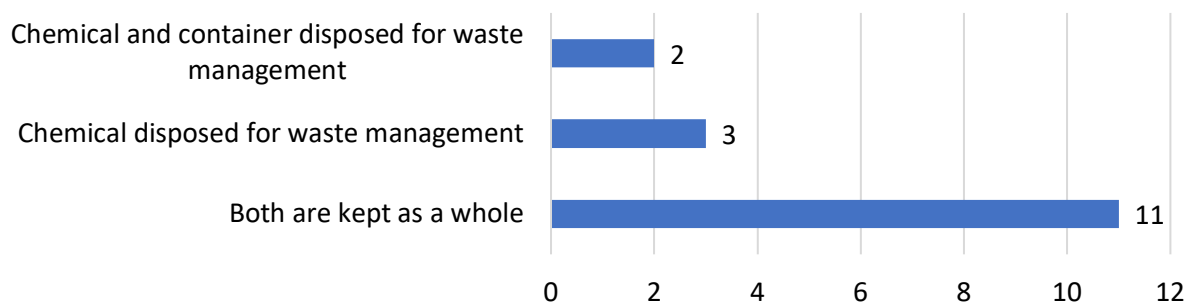
4.1.1. Do you possess any of these chemicals in your collection?



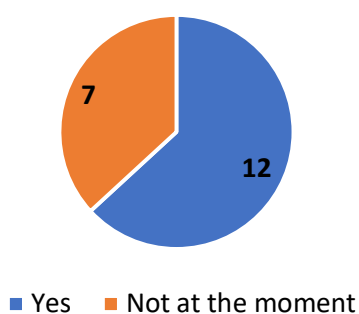
4.1.2. If you answered “Yes” on the previous question, are these chemicals in?



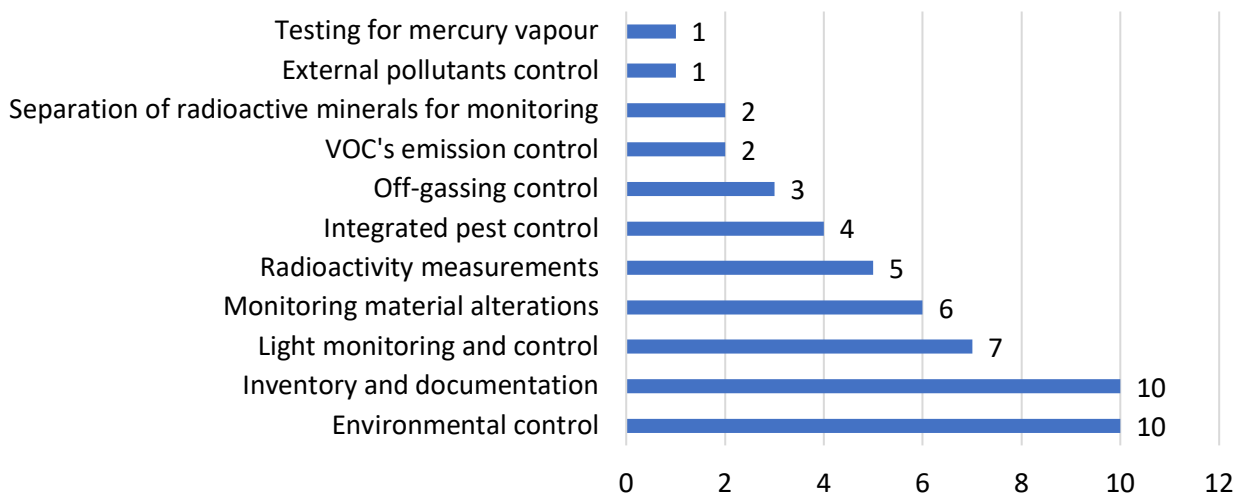
4.1.3. Taking into account the toxic or radioactive chemicals, how are these treated?



4.2. Are there any conservation measures taken for the preventive care of your collection?



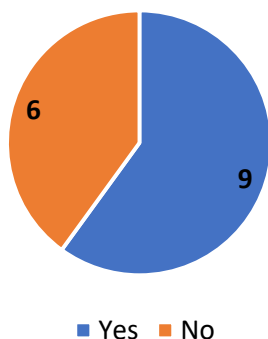
4.3. If you answered “Yes” in the previous question, please check any that apply, and complete when appropriate:



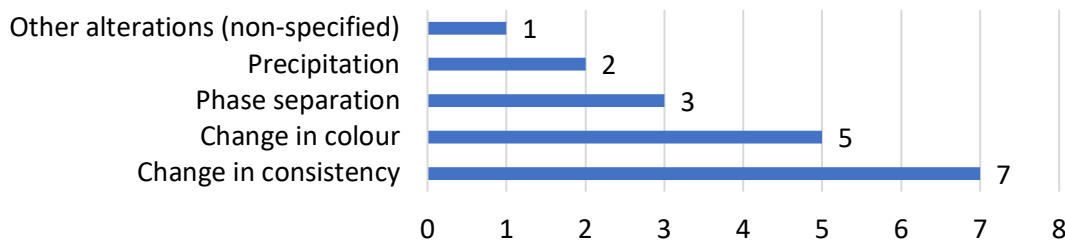
SECTION 5 – OTHER MATERIALS (OPTIONAL)

Although the focus for this work surrounds the deterioration of glass containers, materials such as paper, paints/writing or the chemical itself also present deterioration overtime. In this section, the aim is to understand the material condition for the further development of conservation guidelines.

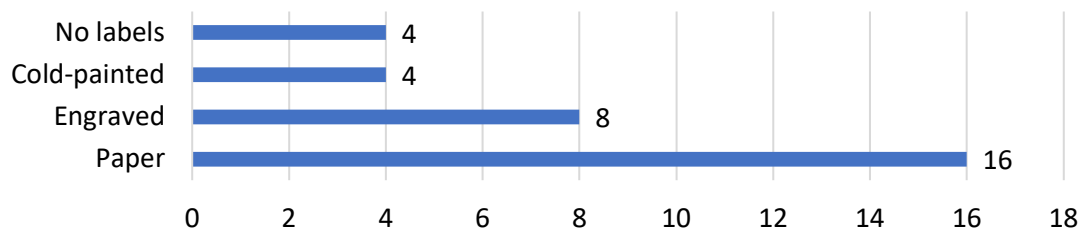
5.1. Regarding the chemical deposited inside the containers, is there any detectable alteration of their normal condition?



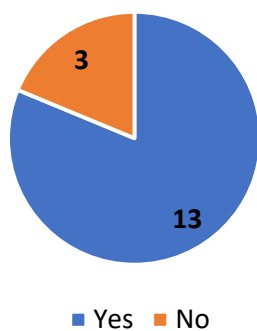
5.1.1. If you answered “Yes” in the previous question, please check all that apply:



5.2. Regarding the labels present in the chemicals of your collection, are these:



5.2.1. Are there any observable damages on the labels?



5.2.2. If you answered “Yes” in the previous question, please check all that apply:

