

UNIVERSIDADE CATÓLICA PORTUGUESA

THE BRONZE SCULPTURE OF SOARES DOS REIS: HISTORY, ANALYTICAL STUDY AND CONSERVATION INDOORS AND OUTDOORS

A ESCULTURA EM BRONZE DE SOARES DOS REIS: HISTÓRIA, ESTUDO ANALÍTICO E CONSERVAÇÃO EM CONTEXTO INTERIOR E EXTERIOR

Thesis submitted to the Universidade Católica Portuguesa
in fulfilment of the requirements for the degree of Doctorate in Conservation and Restoration of Cultural Heritage
by

Pablo Andrés General Toro

ESCOLA DAS ARTES

September 2025



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By Pablo Andrés General Toro

Under the supervision of: Eduarda Vieira, Patrícia Moreira, Carlo Emanuele Bottaini

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To my granny "Mami" Zuny, to my father Tito, and to my little brother Roberto, who remain always in my memory and in my heart.

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ABSTRACT

This doctoral research examines the bronze sculptures of António Soares dos Reis (1847–1889), contextualising their historical production, material characterisation, and conservation challenges. Combining archival research with scientific analysis, the study explores the relationship between Portuguese foundry practices of the 19th and 20th centuries and the present condition of the sculptor's works, both indoors and outdoors.

Archival evidence highlights the role of artistic and industrial foundries that participated in sculpture casting during the 19th century, with particular emphasis on the development of artistic foundries in Vila Nova de Gaia during the 20th century. These institutions played a decisive role in the materialisation of official bronze replicas, ensuring the preservation of works originally conceived in fragile media such as plaster or terracotta.

Analytical campaigns were carried out on a representative group of sculptures preserved in the Museu Nacional Soares dos Reis (MNSR) and located in Porto and Guimarães. Non-destructive and micro-invasive techniques, including X-ray fluorescence (XRF), X-ray diffraction (XRD), optical microscopy (OM), and scanning electron microscopy with energy-dispersive spectroscopy (SEM-EDS), enabled the characterisation of alloys and corrosion products. Results indicate that the sculptures are mostly quaternary bronzes composed of copper, tin, zinc, and lead. Corrosion phases identified include both stable products such as cuprite and brochantite, and more aggressive compounds such as atacamite and nantokite, strongly conditioned by environmental context.

The thesis also reviews conservation methodologies, with special attention to the progressive incorporation of sustainable approaches. Alternatives to traditional products are being

investigated, including new protective coatings and corrosion inhibitors that seek to combine efficacy with lower environmental and health impacts.

By integrating historical documentation, scientific analysis, and conservation practice, this research provides the first systematic technical corpus on Soares dos Reis's bronzes. It demonstrates how foundry practices, alloy compositions, and environmental exposures jointly determine the long-term stability of his works. More broadly, it contributes to the development of methodologies for the conservation of Portuguese bronze sculpture and to ongoing international debates on the sustainable preservation of metallic heritage.

Keywords: António Soares dos Reis, Bronze sculpture, Foundries, Analytical techniques, Alloy characterisation, Corrosion products, Conservation methodologies

RESUMO

Esta investigação doutoral examina as esculturas em bronze de António Soares dos Reis (1847–1889), contextualizando a sua produção histórica, caracterização material e desafios de conservação. Combinando investigação arquivística com análise científica, o estudo explora a relação entre as práticas de fundição portuguesas dos séculos XIX e XX e o estado atual das obras do escultor, tanto em interiores como em exteriores.

A documentação arquivística evidencia o papel de fundições artísticas e industriais que participaram na fundição de esculturas durante o século XIX, com especial destaque para o desenvolvimento das fundições artísticas em Vila Nova de Gaia durante o século XX. Estas instituições desempenharam um papel decisivo na materialização de réplicas oficiais em bronze, garantindo a preservação de obras concebidas originalmente em suportes frágeis como o gesso ou a terracota.

As campanhas analíticas foram realizadas sobre um conjunto representativo de esculturas conservadas no Museu Nacional Soares dos Reis (MNSR) e localizadas no Porto e em Guimarães. Foram aplicadas técnicas não destrutivas e micro-invasivas, tais como fluorescência de raios X (XRF), difração de raios X (XRD), microscopia óptica (MO) e microscopia eletrónica de varrimento com espectroscopia de dispersão de energia (SEM-EDS), permitindo a caracterização das ligas e dos produtos de corrosão. Os resultados indicam que as esculturas são, na sua maioria, bronzes quaternários compostos por cobre, estanho, zinco e chumbo. Foram identificadas fases de corrosão estáveis, como a cuprite e a brocantite, bem como compostos mais agressivos, como a atacamite e a nantokite, fortemente condicionados pelo contexto ambiental.

A tese revê igualmente metodologias de conservação, com especial atenção à incorporação progressiva de abordagens sustentáveis. Estão a ser investigadas alternativas a produtos tradicionais, incluindo revestimentos protetores e inibidores de corrosão que procuram conciliar eficácia com menor impacto ambiental e sanitário.

Ao integrar documentação histórica, análise científica e prática de conservação, esta investigação oferece o primeiro corpus técnico sistemático sobre os bronzes de Soares dos Reis. Demonstra como as práticas de fundição, as composições das ligas e as exposições ambientais determinam em conjunto a estabilidade a longo prazo das suas obras. Num sentido mais amplo, contribui para o desenvolvimento de metodologias para a conservação da escultura em bronze em Portugal e para os debates internacionais sobre a preservação sustentável do património metálico.

Palavras-chave: António Soares dos Reis, Escultura em bronze, Fundições, Técnicas analíticas, Caracterização de ligas, Produtos de corrosão, Metodologias de conservação.

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LIST OF ABBREVIATIONS

APBA	Academia Portuense de Belas Artes (Academy of Fine Arts of Porto).
ASLF	Adelino Sá Lemos Foundry.
AMT	2-Amino-5-mercapto-1,3,4-thiadiazole.
BTA	Benzotriazole.
CINFU	Centro de Formação Profissional da Indústria de Fundição (Professional Training Centre for the Foundry Industry).
DMC	Dimethyl Carbonate.
EBAP	Escola de Belas Artes do Porto (School of Fine Arts of Porto).
EATL	Empresa Artística Teixeira Lopes.
EDDS	Ethylenediamine Disuccinic Acid.
EDTA	Ethylenediamine tetraacetic Acid.
EDXRF	Energy Dispersive X-ray Fluorescence.
EIP	Empresa Industrial Portuguesa.
EIS	Electrochemical Impedance Spectroscopy.
ESBAP	Escola Superior de Belas Artes do Porto (Higher School of Fine Arts of Porto).

FBAUP	Faculdade de Belas Artes da Universidade do Porto (Faculty of Fine Arts, University of Porto).
FTIR	Fourier Transform Infrared Spectroscopy.
GC-MS	Gas Chromatography–Mass Spectrometry.
HEDTA	Hydroxyethylethylenediaminetriacetic acid.
ICP-AES	Inductively Coupled Plasma-Atomic Emission Spectroscopy.
ICP-MS	Inductively Coupled Plasma Mass Spectrometry.
ICP-OES	Inductively Coupled Plasma Optical Emission Spectroscopy.
LIBS	Laser Induced Breakdown Spectroscopy.
LNEC	Laboratório Nacional de Engenharia Civil (National Laboratory for Civil Engineering).
MBI	2-Mercaptobenzimidazole.
MBT	2-Mercaptobenzothiazole.
MET	Metropolitan Museum of Art of New York.
MNAC	Museu Nacional de Arte Contemporânea (National Museum of Contemporary Art).
MNSR	Museu Nacional Soares dos Reis (National Museum Soares dos Reis).
OM	Optical Microscopy.
PHB	Polyhydroxybutyrate.
PIXE	Particle Induced X-ray Emission.
PVA	Polyvinyl Alcohol.
RH	Relative Humidity
SEM-EDS	Scanning Electron Microscopy with Energy-Dispersive Spectroscopy.
SEM-FEG	Field Emission Gun Scanning Electron Microscopy.
TEM	Transmission Electron Microscopy.

VOC(s) Volatile Organic Compound(s)

XRF X-ray Fluorescence.

XRMC X-ray Monte Carlo.

GLOSSARY

Casting

The process by which molten metal is poured into a mould to take the desired shape. In artistic sculpture, casting may be performed in a single piece or in sections, depending on the size and complexity of the work.

Chasing / Finishing

The post-casting stage in which surface imperfections are corrected, seams are removed, and details are refined using chisels, files, and abrasives to achieve the final texture and precision.

Core

The internal mass placed within a mould to create hollow sections in a casting. It supports the mould walls during pouring and defines the internal geometry of the object.

Foundry

A workshop or establishment dedicated to melting and casting metals. In sculpture, it refers to the place where plaster models are transformed into metal sculptures, typically bronze.

Industrial / Artistic / Military Foundry

Classification of foundries according to their primary purpose: artistic foundries specialise in the production of sculptural and ornamental works; industrial foundries focus on mechanical, decorative, or architectural components; and military foundries were originally dedicated to the manufacture of armament and artillery.

Lost-wax casting (cire perdue)

A traditional artistic casting technique in which a wax model is covered with refractory material to form a mould. When heated, the wax melts away, leaving a cavity that is filled with molten metal. It allows for great precision and fine detail.

Mould (mould box / casting box)

A hollow form, usually made of sand, plaster, or refractory material, into which molten metal is poured. In monumental works, the mould may be divided into sections to facilitate casting and demoulding.

Natural and Artificial Patina

A natural patina forms over time through corrosion and environmental exposure, while an artificial patina is intentionally applied using chemical solutions or heat to achieve a desired colour or surface effect.

Replica

A copy of a sculptural work produced with institutional authorisation or supervision, intended to ensure the preservation or dissemination of the original. In the case of Soares dos Reis, official replicas were created under heritage-driven initiatives by museums or public bodies.

Repatination

The process of recreating or modifying an existing patina on a metal sculpture, usually to restore its visual coherence or approximate its original appearance.

Reproduction

A copy of a sculptural work produced outside the institutional framework or without official status. Reproductions are generally commercial or decorative in nature and may differ from the original in size, material, or finish.

Reverberatory furnace

A type of furnace used to melt ferrous and non-ferrous metals, in which heat from burners is reflected from the roof onto the melting chamber. This design ensures uniform heating of the metal and prevents direct contact with the fuel.

Sand casting

A casting process that uses compacted sand to form the mould. It became the most widespread method during the 19th century's industrialisation, as it enabled large-scale and cost-efficient production.

INTRODUCTION

The work of António Soares dos Reis occupies a central place in the history of 19th-century Portuguese sculpture. Trained at a moment of transition between inherited academicism and the opening to new European artistic currents, his production reflects both the technical mastery and the expressive capacity that granted him singular recognition in his time. The material legacy of the sculptor, however, presents particular characteristics that render it especially vulnerable, since a large part of his pieces were conceived in plaster or terracotta, fragile materials highly susceptible to deterioration.

Faced with this situation, during the 20th century academic, museological and governmental institutions promoted the creation of official bronze replicas as a strategy that responded to a dual need: on the one hand, to ensure the preservation of a legacy largely held in fragile materials, and on the other, to enhance the cultural and artistic significance of Soares dos Reis through its materialisation in a more durable and prestigious medium. This process transformed ephemeral models into works of greater permanence, guaranteeing the transmission of the sculptor's legacy and consolidating his recognition in the collective memory.

In this context, the analysis of bronze sculptures makes it possible to gain a deeper understanding of the casting techniques employed and, at the same time, to assess the state of conservation of a heritage whose preservation presents specific challenges. This thesis is situated within this framework, taking the work of Soares dos Reis as a case study to explore both the history of artistic bronze casting in Portugal and current issues related to scientific characterisation and the conservation of bronze sculpture.

Research into bronze sculpture in Portugal has developed only in a limited way and, compared with other heritage fields, is still at an early stage. Significant contributions have been made in the field of archaeometallurgy and in archaeological studies, such as those undertaken at Conímbriga by Jorge de Alarcão and Adília M. de Alarcão in the 1960s, which

marked a precedent in the use of scientific analysis applied to archaeological bronze artefacts. In the case of modern sculpture, however, attention has been more limited and less systematic.

A decisive contribution was made in the 1990s, when the National Laboratory of Civil Engineering (LNEC) carried out a pioneering study on a group of emblematic sculptures, including the Monument to the Marquês de Pombal, the one dedicated to the Duque de Saldanha, and the equestrian statue of King José I in Lisbon, as well as the statues of King Pedro IV, King João VI, and Júlio Dinis in Porto. That research explicitly introduced the use of scientific methodologies to evaluate the state of conservation of bronze works, establishing a first reference in this field. Although those studies did not have sustained continuity, they represent a landmark in the integration of instrumental analysis into the conservation of Portuguese sculpture.

At an international level, research on bronze sculptures has been more numerous and diverse. Methodologies for alloy characterisation have been developed, patterns of corrosion linked to different exposure contexts have been identified, and conservation treatments have been assessed comparatively. These advances have made it possible to construct solid frameworks of reference, whereas in Portugal the field is still in development, limiting the possibility of establishing broader comparisons and of applying protocols based on scientific data.

This situation is particularly relevant in the case of António Soares dos Reis, whose work constitutes an undisputed reference point of Portuguese sculpture. Despite its artistic and symbolic importance, no systematic study had previously been carried out on his bronze sculptures or on the alteration processes that affect them. This thesis addresses that need, proposing an interdisciplinary approach that combines historical and documentary research with the scientific characterisation of the pieces.

The general objective of this thesis is to contribute to the knowledge and preservation of the sculptural work of António Soares dos Reis through the study of his bronze sculptures. To achieve this, several specific objectives are established to:

- document the historical context of production and of the official replicas, considering the role of foundries and of academic, museological and governmental institutions.
- characterise the alloys and corrosion products present in the selected sculptures through different analytical techniques.
- identify alteration patterns linked to both environmental and manufacturing factors.
- expand the scientific corpus available on bronze sculpture in Portugal, establishing a new reference for future research.
- explore the current perception of professionals through an international questionnaire; and to review contemporary methodologies, including sustainable proposals, that could be applied in the conservation of this metallic heritage.

With this combination of objectives, the research seeks to connect the historical with the scientific and methodological dimensions, offering more comprehensive knowledge and a sound basis for the informed preservation of heritage of great cultural significance.

The first part of the thesis, comprising Chapters 1 to 3, establishes the historical and contextual framework that makes it possible to understand the object of study in depth. This initial path is essential, since bronze sculpture, both in Portugal and in Europe, was marked during the 19th and 20th centuries by technical, industrial and institutional transformations that directly conditioned the production and conservation of the works. Understanding these dynamics is indispensable for situating the trajectory of António Soares dos Reis in its proper dimension and for explaining the circumstances that led to the production of official bronze replicas, which today constitute the material basis of the corpus analysed.

The first chapter addresses the evolution of bronze sculpture in Europe and Portugal during the 19th and 20th centuries, with particular attention to the ways in which technical advances, industrialisation processes and the consolidation of the artistic bronze-casting profession shaped the development of the medium. It also reviews historical antecedents that, since the Renaissance, contributed to the configuration of a specific language in bronze casting, as well as the circulation of knowledge and models that connected Portuguese workshops with those of Europe. This trajectory shows that the context in which Soares dos Reis worked cannot be understood in isolation, but rather as part of a network of technical

and cultural exchanges that influenced both the production and the reception of bronze sculpture in Portugal.

The second chapter focuses on the sculptural practice of Soares dos Reis and on the description of the techniques he employed in his artistic activity. The creative process began with the sketch, which allowed the definition of the idea and the establishment of the general proportions of the work. From there, modelling in clay was developed, followed by the production of plaster models, which constituted the basis from which moulds could be made and, in some cases, later materialisations in bronze. This part of the chapter describes the sequence of operations, the materials used and the technical solutions that shaped his production, underlining the importance of plaster as an intermediate support and as a vehicle for the preservation of his legacy.

The analysis is complemented by the study of how António Teixeira Lopes in Portugal, Augustus Saint-Gaudens in the United States and Auguste Rodin in France applied comparable artistic techniques. This comparative perspective makes it possible to situate the work of Soares dos Reis in an international framework, highlighting affinities and differences in the sculptural methods employed in the final quarter of the 19th century.

The chapter also includes the study of bronze casting, described from a technical point of view. The moulding, casting and finishing procedures that enabled the transformation of plaster models into metallic sculptures are detailed, explaining the fundamental phases of a process that linked artistic conception with the definitive materialisation of the work.

The third chapter broadens the perspective to the history of artistic bronze casting in Portugal during the 19th and 20th centuries, situating the role of the main foundries and of the institutions that promoted the official production of bronze sculptures by Soares dos Reis. These initiatives came from academic, museological and also governmental entities, which recognised the need to ensure the transmission of a legacy preserved mainly in plaster and terracotta. A clear distinction is also made between the official replicas, produced under institutional support and with legal backing, and the reproductions carried out outside this framework by foundries and firms such as Casa Baganha. While the former responded to a heritage-driven purpose, the latter were directly connected to the art market and to private

demand. The combined analysis makes it possible to understand the coexistence of two modes of production which, although divergent in their aims, configure the current material panorama of bronze sculpture attributed to the sculptor.

The second part of the thesis, comprising Chapters 4 to 6, constitutes the scientific and analytical core of the work. It presents and discusses the results obtained through the application of instrumental characterisation techniques to the selected bronze sculptures. Its purpose is twofold: on the one hand, to document rigorously the elements that constitute the alloys of the sculptures studied, and on the other, to offer a critical interpretation of the factors that affect their conservation. This approach makes it possible to understand how technical decisions in the formulation of bronzes condition the subsequent behaviour of the sculptures in relation to corrosion processes.

The fourth chapter is devoted to presenting the analytical techniques employed. The principles, scope and limitations of methods such as X-ray fluorescence (XRF), X-ray diffraction (XRD), optical microscopy (OM) and scanning electron microscopy with energy-dispersive spectroscopy (SEM-EDS) are described. The inclusion of this section responds to the need to provide the reader with a clear framework to facilitate understanding of the results presented in the following chapters and to enable a critical assessment of their scope. In the Portuguese context, the National Laboratory of Civil Engineering (LNEC) played a pioneering role in the 1990s by applying instrumental analysis to the study of bronze sculptures, with the aim of characterising their alloys and corrosion processes and evaluating the pertinence of possible interventions. This experience constituted a precedent in the integration of scientific techniques into the conservation of modern sculpture in Portugal. At present, these methodologies have been developed at the HERCULES Laboratory, which was responsible for the analyses included in this thesis. The chapter therefore acts as a bridge between the historical dimension and scientific analysis, underlining the central role of instrumental characterisation in this research.

The fifth chapter presents the results of the analysis of the selected sculptures. The criteria that guided the choice of corpus are explained, as well as the practical limitations derived from access to the works and the way in which the different techniques were applied to each

piece. The data, presented in the form of tables, graphs and images, establish a coherent overview of the composition of the alloys and of the corrosion products present in the pieces. One of the main contributions of this chapter is the identification of clear differences between the sculptures cast during the lifetime of Soares dos Reis and the replicas produced in the second half of the 20th century. While the former are characterised by a significant tin content, the latter present much lower proportions of this element, and even its absence, in favour of compositions closer to copper with small amounts of zinc and lead. This finding makes it possible to recognise trends in casting practices and to relate them to the long-term response of sculptures to alteration processes.

The sixth chapter develops the interpretation of corrosion processes and alteration products identified in the sculptures. Based on the data obtained from instrumental analysis, the different typologies of deterioration observed are examined, ranging from the formation of chlorides to the appearance of carbonates and oxides, relating them to the specific exposure conditions of each work. The chapter highlights the interaction between the formulation of alloys, casting processes and environmental factors, showing how each of these elements influences the evolution of corrosion products.

It is emphasised that, although Portugal is a relatively small country, it presents great geographical and climatic diversity that directly affects the conservation of bronze sculptures. Coastal areas are affected by salinity, urban areas by atmospheric pollutants, and rural areas are characterised by greater environmental purity that determines other alteration patterns. This panorama highlights the importance of analytical knowledge as a basis for designing adapted diagnoses and conservation decisions adjusted to each context.

The third part of the thesis, comprising Chapters 7 and 8, turns attention to professional practice and to the methodologies currently employed in the conservation of bronze sculptures. Having addressed the historical context and the results of scientific analysis, this section examines how that knowledge interacts with professional strategies and with the possibilities for innovation arising from contemporary research.

The seventh chapter presents the results of an international questionnaire addressed to conservator-restorers, designed to gather information on the most widespread methods in the

treatment of bronze sculptures. The survey was organised into thematic blocks that covered a broad range of issues: the identification of the most frequent alterations; the types of intervention applied, from cleaning to repatination, corrosion inhibitors and protective coatings; the materials and products commonly used; preventive conservation strategies, including maintenance plans, monitoring and systematic documentation; and a specific block devoted to sustainability, aimed at assessing the substitution of toxic products, waste management and the adoption of less aggressive alternatives.

The results reveal a heterogeneous panorama, in which consolidated methodologies coexist with adaptations developed according to the needs of each institution, country or environmental context. This diversity reflects the richness of accumulated experience, while also evidencing the difficulty of achieving broad consensus on certain procedures. Beyond these differences, common concerns emerge that guide professional practice: the need to ensure the stability and reversibility of treatments, the importance of documenting interventions systematically, and the desirability of incorporating preventive strategies that reduce the frequency of direct interventions.

The eighth chapter offers a review of contemporary techniques for the conservation of bronze sculptures. The most widely used cleaning procedures are analysed, together with corrosion inhibitors of both traditional and new generations, as well as protective coatings applied in different contexts, ranging from acrylic lacquers to synthetic resins and high-performance polymers. Attention is also given to preventive conservation strategies, increasingly regarded as essential for prolonging the stability of interventions. Alongside these consolidated techniques, the chapter also considers emerging proposals with a more sustainable profile, such as biopolymers, amino acids and plant extracts. Although still at a validation stage, these alternatives form part of an expanding debate that seeks to integrate technical efficacy, environmental responsibility and professional safety.

With this third part, the thesis links the historical and scientific results obtained in the previous chapters with current professional practice and with the research lines that are emerging for the future. It thus shows that the study of the work of António Soares dos Reis transcends the analysis of a specific corpus, becoming part of broader debates within the

discipline, in which historical documentation, scientific characterisation and methodological reflection converge.

Taken as a whole, this thesis approaches the bronze sculpture of António Soares dos Reis from a dual perspective: historical and analytical. By bringing together these two dimensions, it seeks not only to broaden knowledge of the conditions of production and preservation of his works, but also to highlight the value of scientific analysis as a tool applicable in conservation-restoration. This approach situates the sculptor's legacy within a framework that connects the artistic and technical practices of his time with the current challenges of preserving metallic heritage.

The contribution of the thesis is defined in terms of both method and scope. From a methodological point of view, it combines documentary research with instrumental techniques and with the observation of professional practice, articulating an interdisciplinary approach consistent with the complexity of the object of study. In terms of results, it contributes to enriching the scientific corpus on bronze sculpture in Portugal, a field that until now has had a limited basis, by providing new data and by integrating complementary historical and analytical perspectives.

The research is also set within a context of transformation in conservation-restoration, in which it is necessary to reconcile the technical efficacy of treatments with attention to environmental contexts and with the gradual adoption of more responsible methodologies. In this sense, it documents a singular case, while linking it to international debates that are currently guiding the discipline towards more precise diagnoses, better-grounded interventions and the progressive integration of sustainability criteria.

Finally, this thesis reinforces the dialogue between history, science and conservation, showing that the interaction of these perspectives constitutes a reliable path for ensuring the preservation and appreciation of bronze heritage in the future.

PART I HISTORY, PRACTICE AND MATERIALISATION OF BRONZE SCULPTURE AROUND SOARES DOS REIS

CHAPTER 1. THE PRODUCTION OF BRONZE SCULPTURES IN EUROPE AND PORTUGAL

1.1 INTRODUCTION. CONTEXTUAL BACKGROUND: THE DEVELOPMENT OF ARTISTIC BRONZE CASTING IN EUROPE

This section examines the revival of artistic bronze casting in 19th-century Europe, which played a crucial role in shaping the production of bronze sculptures across the continent, including Portugal. Although this revival was significant, it is important to recognise the long-standing tradition of bronze casting in Italy, which dates back to the early Renaissance.

During the Renaissance, bronze was primarily used for bells and cannons, with sculptural production being relatively limited (F. Bewer, 1996). Notable exceptions include Lorenzo Ghiberti's *North Door* (1403–1424) and the *Gates of Paradise* (1425–1452) for the *Florence Baptistery*, as well as Donatello's *David* (c. 1440), the first male nude sculpture since antiquity, and the equestrian statue of the *Condottiero Gattamelata* (1444–1453), cast using the lost-wax technique (Hatje, 1995).

The 16th century witnessed advancements in large-scale bronze reproduction, alongside a growing trend for reduced versions of iconic monuments. This fostered the rise of a bronze casting industry, notably in the workshops of Giambologna, which were highly active in the

latter half of the century (Draper, 2002). However, the 17th and 18th centuries saw a decline in artistic bronze casting, with a resurgence occurring in the early 19th century, driven by the establishment of prominent foundries throughout Europe and an increased public interest in bronze artworks (Rich, 1988).

Despite the high cost and technical challenges associated with bronze casting, the industry continued to evolve. The migration of skilled founders from France, Italy, and the Netherlands to countries like England contributed to this development (Sullivan, 2005). Throughout the 17th and 18th centuries, monumental bronze sculpture was predominantly commissioned to commemorate military and political figures, as evidenced by equestrian statues such as those of Philip III (1616) and Philip IV (1640) in Madrid, Charles I (1633) in London, and Louis XIV (1692) and Louis XV (1766) in Paris (Castelle, 2016; Sullivan, 2005), although the equestrian statues of Louis XIV and Louis XV were destroyed during the French Revolution. Other notable works include the equestrian statue of King Frederick V of Denmark (1771) in Copenhagen and the Quadriga of Victory at the Brandenburg Gate in Berlin (1793)

Publications documenting the casting process of these sculptures contributed to knowledge transfer across Europe. For instance, Germain Boffrand (1743) provided a detailed account of the casting of Louis XIV's equestrian statue, while Pier Jean Mariette (1768) described the process behind the equestrian statue of Louis XV. These texts served as technical references for sculpture casting in Portugal, where Joaquim Machado de Castro erected the grand equestrian statue of King José I in 1775. Machado de Castro himself documented the process in a publication that remains a valuable historical source (Machado de Castro, 1810).

The resurgence of bronze sculpture production in the 19th century marked a turning point, laying the foundation for industrialised artistic casting. This development set the stage for Portugal's entry into the field, albeit at a slower pace compared to other European nations. The following sections explore this evolution, focusing on the industrialisation of bronze casting, the persistence of lost-wax techniques, and the eventual establishment of art foundries in Portugal.

1.2 THE INDUSTRIALISATION OF ART CASTING THROUGH SAND CASTING IN THE 19TH CENTURY

At the beginning of the 19th century, artistic bronze casting experienced a revival across Europe, particularly in France, where industrial and social changes significantly contributed to its development (Beentjes, 2019; Pouyet et al., 2019; Voillot, 2014). The abolition of the guild system in 1791, a consequence of the French Revolution, played a pivotal role in modernising production and facilitating technological progress in foundries (Voillot, 2014).

This industrial breakthrough was evident through the integration of innovative materials and techniques, with large-scale casting standing out as one of the most significant achievements. One of the most significant innovations during this period was the refinement of sand casting, which allowed for the large-scale production of bronze sculptures (Voillot, 2014).

The implementation of large-scale casting had a significant impact on the efficient distribution of these artifacts in both the French and international markets. This phenomenon, in turn, played a crucial role in boosting demand for creations made in France, enabling not only the elite but also broader segments of society to access these valuable productions. This dynamic contributed to positioning France prominently in the realm of artistic casting, particularly in the context of small-scale sculptures and decorative metal ornaments (Janson, 1985; Lebon, 2020).

The reputation earned by French foundries extended to other territories. Records from as early as 1836 already indicate the presence of French casting experts in the United Kingdom, with a second wave of foundrymen arriving after the fall of the Paris Commune in 1871 (Simon, 2017; Whatmore, 1995). By the late 19th and early 20th centuries, France had firmly

established its position as an international leader in bronze sculpture production (Lebon, 2020; McWilliam, 1997).

The increasing demand for bronze sculptures led the proliferation of specialised workshops and the establishment of professional collaborations among artisans and foundries. This culminated in the formation of the *Réunion des Fabricants de Bronze*, an organisation that regulated the profession, established legal frameworks, and enhanced the influence of foundries within the French artistic landscape (Voillot, 2014).

The industrialisation of bronze casting marked a significant shift in artistic production. While sand casting became the preferred method for large-scale works due to its efficiency, other European regions continued to employ traditional techniques, as explored in the following section on Italy and the revival of lost-wax casting.

1.3 REVIVAL OF LOST-WAX CASTING IN ITALY AND FRANCE

In contrast to the French context, Italy maintained small-scale production using the lost-wax casting method. This process was known for being more expensive and labour-intensive than the sand-casting technique, and its inherent unpredictability did not align with the demands for agility and mass production, requirements frequently encountered in an increasingly industrialised society (Hecker, 2019; Lebon, 2020).

In other parts of Europe, the use of the lost-wax casting technique was limited due to the reasons mentioned above. In fact, in France, Honoré Gonon's foundry was the only enterprise that employed this technique in the period between 1829 and 1871 (Lebon, 2020).

However, over time, the lost-wax casting technique experienced a surge in popularity, largely due to its artisanal qualities and its status as an ancient method. This phenomenon occurred in a context where the Industrial Revolution exerted a profound influence on daily European life, particularly in urban areas, fostering a renewed appreciation for skilled craftsmanship and refined artistic expression. Simultaneously, industrial advancements allowed for the optimisation of the lost wax casting process, mitigating many of the risks historically associated with this method. This convergence of factors turned Italy into a focal point of attention for both foundries and sculptors.

As is typical in such cases, it was the more privileged socio-economic groups that initially showed a keen interest in this type of casting technique. The use of the lost-wax casting technique conferred distinction and prestige on the pieces, resulting in finely executed finishes. In the case of the late French monarchy, as noted by Lebon (2020), the aura of a "secret technique" and the ties to the classical roots of lost-wax casting imbued the process with a certain romantic appeal. Consequently, the rulers of the time chose this method to support their commemorative and artistic endeavours. As expected, the popularity of works produced using this technique soon spread from elite circles to the burgeoning bourgeoisie.

In this context, Italy, acknowledged as the birthplace of lost-wax casting, became the artistic epicentre for mastering the technique. This prominence continued until the early 20th century, when Paris emerged as the new centre of artistic foundry work (Wiegartz, 2020). Italian cities with stablished foundries, particularly Rome, Florence, and Naples, became destinations for sculptors seeking to learn the method. Furthermore, many Italian-born foundry workers migrated across Europe joining existing workshops or founding their own. This migratory movement to other countries persisted, in some cases, until the outbreak of the Second World War, as evidenced in the United Kingdom (Simon, 2017).

A compelling example of sculptors' eagerness to engage directly with the lost-wax technique is that of the German sculptor Georg Kolbe (1877-1947). Kolbe personally cast his

equestrian statue *Sieger* (Conqueror) in 1899 employing this method in a small foundry he had rented near St. Peter's Square in Rome (Wiegartz, 2020).

By the end of the 19th century, Kolbe and other artists across Europe were actively encouraging local foundries to offer lost-wax casting services. The adoption of this technique prompted numerous companies to undergo significant transformations, incorporating sculpture production as a core element of their business models and enhancing their institutional prestige. One such example is the *Compagnie des Bronzes* (1854 – 1979), based in Brussels, which experienced its period of greatest prosperity during the 1880s thanks to the integration of lost-wax artistic casting into its repertoire (Dupont, 2004).

Works produced using the lost-wax technique stood out for characteristics that made them widely valued and highly sought after. These included exceptional quality, meticulous workmanship, and refined finishes. Moreover, their distinctive character lay in their exclusivity. Some of these pieces also featured elegant patinas, which added aesthetic value and elevated them to the status of objects of art.

A prime example highlighting the value of this casting method in the European art market at the start of the 20th century is the establishment of the Hébrard Foundry in Paris (1904–1937). This firm elevated lost-wax castings to the category of luxury objects. Adrien-Aurélien Hébrard (1865–1937), a member of the French elite, recognised a lucrative business opportunity in such works. His foundry's creations gained renown for their exceptional craftsmanship and superb patinas, which conferred a distinctive character upon each piece (Lebon, 2020).

Among the numerous creations produced by the Hébrard Foundry, the casting of the bust of João Marques de Oliveira in 1926 stands out. Sculpted by Soares dos Reis in 1881, this bust is one of the works examined in the present study.

1.4 HISTORY OF ARTISTIC BRONZE CASTING IN PORTUGAL: FROM MILITARY FOUNDRIES TO ART FOUNDRIES

The art casting industry in Portugal is considered relatively recent, with the first specialised companies in this activity dating back to the early 20th century. However, despite its relative novelty, sculptures of national significance were cast in the country during the 18th and 19th centuries. Initially, this task fell under a military-oriented foundry, and later, from the mid-19th century onwards, some industrial foundries took on this role until around 1910 when the first art-specialised foundry emerged.

Despite the number of cast pieces in Portugal during the 18th and 19th centuries, there is a scarcity of written sources detailing the processes and anecdotes that took place during casting. In this regard, the most notable sources include Joaquim Machado de Castro's detailed report on the construction of the equestrian statue of King José I of Portugal (Machado de Castro, 1810), as well as a report compiled by Tomás Nunes and a Minute Book detailing the administrative and technical process of casting the statue of King Pedro V in Porto (Comissão do Monumento a D. Pedro V, 1861, 1866).

1.4.1 18th Century: The Foundry of the *Arsenal Real do Exército* and the casting of the Equestrian Statue of King José I of Portugal

The foundry of the *Arsenal Real do Exército* (Royal Arsenal of the Army) was the first Portuguese institution to cast bronze sculptures in Portugal, despite not being originally created for this purpose. It was commissioned around 1515 by King Manuel I (1469-1521) and was known as *Tercenas de Porta da Cruz*. The foundry was located at the site currently occupied by the Military Museum of Lisbon. In addition to the foundry, the building also

housed a gunpowder factory and storage facility. Its primary task was to produce and store artillery, and it included a musket workshop (Pinto, 2009).

During the reign of King João III (1521 – 1577), the *Tercenas de Porta da Cruz* was expanded, absorbing some private foundries, and becoming known as *Fundição da Coroa de Portugal* (Foundry of the Portuguese Crown). Between 1540 and 1764, the foundry increased in size and importance, changing its name to *Tenência Geral da Artilheria* (also known as *Fundição dos Castelhanos* during the Spanish rule over Portugal), and finally to *Arsenal Real do Exército* in 1764 (Mello, 1939; Pinto, 2009).

In 1758, Bartolomeu da Costa[1], High Constable of the Court Garrison, became an adjunct to the *Tenência Geral da Artilharia*. Da Costa was a prestigious founder of military equipment and played a vital role in the casting of the equestrian statue of King José I of Portugal. At the *Tenência Geral da Artilharia*, Da Costa was responsible for developing the foundry, which, up to that point, lacked an active foundry and skilled workers for casting. There was only a small building where bells had been cast in the past (Lima, 1975; Mello, 1939).

In addition to creating the equestrian statue of King José I, the foundry of the *Arsenal Real do Exército* cast other pieces during the 19th and early 20th centuries. Among them, this institution cast the statues of Pedro Alexandrino da Cunha (Luanda, 1871), José Estevão (Aveiro, 1888), the monument to Afonso de Albuquerque (Belém, 1902), the statue of Fernandes Tomás (Figueira da Foz, 1909), and the Monument to Bishop Antonio Alves Martins (Viseu, 1911) (Revista do Occidente, 1889, 1902, 1909, 1911).

[1] Bartolomeu da Costa was born in Belém, Portugal on November 1, 1731. He enlisted in the Marine Artillery in 1744 at the age of 13, experiencing a successful military career and being appointed Lieutenant General of the Army in 1796. He led the *Fundição de Cima* (1762) and the iron foundry at *Paço dos Arcos* (1778). Da Costa was also a founding member and treasurer of the Portuguese Royal Academy of Sciences (1779) and Superintendent of iron mines and all coal mines in the Kingdom of Portugal (1782). Bartolomeu da Costa died in 1801. (Mello, 1939).

The Casting of the Equestrian Statue of King José I of Portugal

The bronze casting of the equestrian statue of King José I marks a milestone in the history of artistic casting, as it is the first sculpture cast in Portuguese territory and notable for the monumental size of the work, cast in a single piece using the lost-wax technique. Despite Joaquim Machado de Castro being well-known for creating the equestrian statue of King José I, the importance of Bartolomeu da Costa as the founder of the work is undeniable. After Machado de Castro was chosen, among other participants, to create the statue of the monarch, Da Costa was called upon to oversee the casting process.

The monument, commissioned by the *Marquês de Pombal*, represented a milestone in national casting, both for its novelty, the technique employed, and its difficulty. The creation of this piece earned Machado de Castro great recognition as the creator of the first monumental sculpture made in Portugal. Likewise, Colonel Bartolomeu da Costa, for the monumental single piece lost-wax casting, was appointed Superintendent of the Artillery Foundries and Laboratory of War Instruments of the Kingdom of Portugal (Mello, 1939).

For the modelling of the statue, Machado de Castro relied on documentary sources about the creation and casting of monumental equestrian statues, through which he gained extensive knowledge on the subject. The main publications at the time in this area originated from France. Machado de Castro mentioned drawing inspiration from publications on the creation of the equestrian statues of Louis XIV [2], published in 1743; the equestrian statue of Louis XV[3], and the equestrian statue of Frederick V in Copenhagen[4].

[2] The equestrian statue of Louis XIV was modeled by François Girardon in 1685 and cast by the Keller Foundry in Paris in 1692. The statue was in the current Place Vendôme until it was destroyed in 1792 during the French Revolution.

[3] The equestrian statue of Louis XV was sculpted by Edme Bouchardon in 1747 and cast by the foundryman Pierre Gor at the Arsenal de Paris in 1758. The statue, situated in the present-day Place de la Concorde, was destroyed in 1792 during the French Revolution.

[4] The equestrian statue of Frederick V was sculpted by Jacques Saly in 1768 and cast by Pierre Gor in 1771.

At the time of casting the statue, the foundry had three reverberatory furnaces for cannons, constructed with refractory bricks. Each of these furnaces had a capacity of 32.5 tonnes of liquid metal (Lima, 1975; Mello, 1939).

The casting was carried out on 15 October 1774, with 12 workers. A total of 38,564 kilograms of bronze were used for the casting, which took 28 hours to melt. The mould of the statue was filled in 7 minutes and 53 seconds. The final work measures 6.93 meters and weighs 35,245 kilograms. The statue was placed in the centre of *Terreiro do Paço* on 20 May 1775, and inaugurated on 6 June of the same year, the anniversary of the King's birth (Mello, 1939).

In addition to being the first large-scale sculpture cast in Portugal, the equestrian statue of King José I was considered a landmark as it was cast using the lost-wax technique in a single piece, given the monumental size of the work and its difficulty. This type of casting, previously executed based on the references that Machado de Castro relied upon, required great expertise on the part of the founder. It was a risky decision, considering that Da Costa could have cast the statue in multiple pieces using the sand-casting technique, a method he was well-versed in due to his experience in casting weaponry.

1.4.2 19th Century: Industrial Foundries

Although industrial progress was made in Portugal, the country's development was hindered by various circumstances. The revolution in Porto in 1820 affected commercial and trade activities, while the political instability of the 19th century had a negative impact on the country's pre-industrial system. These socio-economic challenges affected financial support from banking institutions for the industry and limited new investments by companies (Cordeiro, 1996; Serrão, 1995). Consequently, although there was an 80% increase in the creation of industries in the Porto area between 1845 and 1852, these companies were small-scale and focused on manufacturing (Cordeiro, 1996).

Despite the aforementioned challenges, there was a gradual influx of foreign capital that fuelled industrial growth in Portugal. In 1863, a branch of the New London & Brazilian Bank was established in Porto, laying the groundwork for the arrival of other banks, which by 1878 totalled nine financial entities. These foreign investments stimulated economic development and improved maritime and land communications, triggering a rivalry between

Porto and Lisbon in terms of commercial and naval dominance in Portugal (Serrão, 1995). In the case of Porto, this business boost was particularly significant due to the British community. These investments were specifically directed towards improving urban and suburban transportation, as well as strengthening the metallurgical industry in the city (Queiroz, 2001; Serrão, 1995).

With regard to the metallurgical industry, it experienced a significant boost with the introduction of the steam engine by the British, who, along with the Portuguese and Germans, contributed capital to this industrial sector (Queiroz, 2001). By 1852, there were already eleven metal foundries in the country, located in Lisbon (five), Porto (five), and Aveiro (one), employing a total of 680 people, including 143 minors. These foundries had a total of sixteen steam engines, distributed between Lisbon (eleven) and Porto (five). By 1881, the number of foundries had increased to fifteen (Comissão Central Directora do Inquérito Industrial, 1883).

Among the fifteen metallurgical companies, the *Perseverança*, *Empresa Industrial Portuguesa*, and *Massarelos* foundries stood out for their scale, production volume, and number of employees. These industrial foundries distinguished themselves as the only ones that carried out sculpture casting work during the 19th and 20th centuries in Portugal. However, examples of works cast by these companies were scarce, as the main foundry for sculptures in Portugal continued to be the foundry of the *Arsenal Real do Exército*, mentioned in the previous subchapter.

The *Perseverança* Foundry was established in 1809 by José Pedro Collares. For a considerable period, the company remained under its owner's name until, in 1850, a transition occurred involving the control and management by its descendants. Subsequently,

there was a change in the foundry's name, adopting the name *Perseverança*, after one of the founder's sons, José Pedro Collares, acquired ownership of the company in 1858 (Comissão Central Directora do Inquérito Industrial, 1881b).

The foundry was located at Largo de Conde Barão 14, in the *Bairro Alto* district of Lisbon. This foundry was known for its specialisation in working with metals such as copper, bronze, iron, and lead. The products manufactured from these materials primarily served the food industry, agriculture, and domestic purposes. It is noteworthy that the foundry had the merit of being the pioneer in Portugal in the production of steam engines and other supplies that typically had to be imported from other countries (Comissão Central Directora do Inquérito Industrial, 1881b).

At the time of its establishment, the company had one worker. However, its growth was remarkable, reaching a workforce of one hundred and forty individuals in 1854. By 1881, already well-established in its trajectory, it had a total of two hundred and forty employees working a ten-hour workday. The *Perseverança* Foundry gained significant reputation in the country's industrial scene, recognised as the only national company capable of successfully competing with its foreign counterparts (Comissão Central Directora do Inquérito Industrial, 1881b).
Regarding the acquisition of raw materials, *Perseverança* Foundry chose to import them from other countries, formulating the metal alloys within its own workshops; for instance, lead was sourced from Spanish suppliers due to its high cost in Portugal (Comissão Central Directora do Inquérito Industrial, 1881b).

Among the artistic pieces produced by *Perseverança* Foundry, the monument dedicated to Camões stands out, inaugurated in the city of Lisbon in 1867 (Raposo, 1987).

The *Empresa Industrial Portuguesa* (EIP) was established in Lisbon in 1874 by entrepreneur João Burnay. Initially, this foundry was headquartered in the *Palácio das Janelas Verdes*, which was once the residence of the renowned Marquês de Pombal. However, in 1876, the foundry was relocated to the Santo Amaro area, on land owned by the Marquês de Sabugosa (Comissão Central Directora do Inquérito Industrial, 1881b).

The Industrial Inquiry of 1881 does not provide evidence that EIP was also involved in the production of artistic objects. However, in its facilities, the foundry carried out the casting of sculptures destined for monuments. Examples of this include the statue for the monument to the Duke of Terceira (Lisbon, 1877), the bust dedicated to José Cinatti (Évora, 1882), and the commemorative bust of *Francisco de Almada e Mendonça* (Porto, 1885), modelled by Soares dos Reis in 1883.

In 1881, the EIP foundry had two hundred employees working nine hours a day in the manufacturing of metal coverings, steamboats, bridges, and pipelines. Raw materials were sourced from abroad. In the description of materials acquired, as recorded in the Industrial Inquiry of 1881, purchases of bronze or brass are not mentioned, though zinc and lead are, suggesting that the foundry formulated its metal alloys in-house (Comissão Central Directora do Inquérito Industrial, 1881b, p. 219).

The *Massarelos* foundry originated in 1850, thanks to the vision of William Hawke, in partnership with Joaquim Lidoro de Castro and Joaquim Augusto Kopke Schwerin de Sousa, Baron of *Massarelos*. Hawke played a crucial role in introducing English technology to the factory. Two years later, in 1852, the foundry merged with other partners and became part of the industrial conglomerate known as *Aliança* (Queiroz, 2005).

The *Massarelos* foundry was located at Rua Basílio Teles 62, on the riverside of the Douro River in Porto. This company stood out for its thriving production, specialising in cast iron manufacturing. By1881, it had a workforce of two hundred and twenty workers, who were engaged in various projects, including the manufacturing of steam machinery, canopies for train stations, hydraulic lifts, steamboats, grain mills, and greenhouses (Comissão Central Directora do Inquérito Industrial, 1881a).

In 1906, the business conglomerate *Aliança* experienced significant growth by expanding through the acquisition of *Fundição do Ouro*. The *Massarelos* foundry, on the other hand, continued its operations uninterruptedly until 1975 when it finally ceased its activity.

Although it is easy to discover numerous examples of the work of the *Massarelos* foundry in terms of architectural structures, ornamental pieces, and household items, finding sculptures produced by this foundry is a more complex task.

In this regard, it is widely recognised that the company carried out the bronze casting of the iconic statue of *King Afonso Henriques* in Guimarães in 1887, as well as the creation of an iron replica in 1940, that was erected at the *Beneficência Portuguesa* Hospital in Rio de Janeiro.

Prior to the casting of the aforementioned statue by Soares dos Reis, there was at least one earlier initiative to cast a sculptural piece. This involved an iron bust in honour of King Pedro V of Portugal, who died in 1860. The project was initiated in 1861 by a military commission that organised a donation campaign to fund the creation of the statue (Carvalho, 1861). However, this project did not come to fruition.

Throughout the 20th century, the *Massarelos* foundry continued to cast sculptures in iron. Images of one of these creations are preserved in the Municipal Archive of Porto, which was presented at the Permanent Exhibition of Iron Architecture in 1969[5].

1.4.3 The ephemeral foundry on Rua Malmerendas and the creation of the statue of King Pedro V of Porto

The presence of a foundry exclusively dedicated to the casting of a sculpture is uncommon. The Rua Malmerendas foundry emerged from a unique situation, where a lack of financial resources for the project and the absence of expertise in artistic casting in Portugal converge. Unlike countries such as France, Italy, the United Kingdom, Germany, and Belgium, which

[5] Arquivo Municipal do Porto: F-NP/CMP/4/6922; F-NP/CMP/4/6923; F-NP/CMP/4/6925; F-NP/CMP/4/6926; F-NP/CMP/4/6929

already had internationally recognised artistic foundries in the 19th century, a similar enterprise had not yet been established in Portuguese territory.

The conception of the project for the monument to King Pedro V is meticulously described in the documents *Relatório dos trabalhos da Comissão que levantou o Monumento ao Senhor D. Pedro Quinto na Praça da Batalha (1866)*, *Atas da Comissão Administrativa, do monumento artístico a D. Pedro V* (1863), and *Atas da Comissão dos Artistas do Monumento a D. Pedro V* (1866), which are preserved in the Municipal Archive of Porto.

The plan to erect a monument in honour of King Pedro V emerged on 21 November 1861, driven by a group of forty-three individuals from the artistic, intellectual, and industrial circles of Porto. They formed a commission to coordinate the initial steps of creating a commemorative statue in honour of the young monarch, who had passed away on the 11th of that same month.

The funding for the project was achieved through *subscrições*[6] in Portugal and Brazil. However, this method did not manage to raise a significant amount due to the economic difficulties affecting not only the region but all of Europe. The cotton industry[7], an influential force in the city, was in crisis, limiting financial support. Despite this, the project was

[6] The *subscrições* system is a donation system where individuals and institutions are requested to contribute money to cover the expenses of a project. This type of funding is observed in projects for other significant sculptures in Portugal in the 19th century, such as the monument to Camões in Lisbon or the monument to D. Afonso Henrique in Guimarães. Sometimes, the inability to raise enough to fund the project would cause delays that could span several years.

[7] The Cotton Famine, or crisis of the cotton industry, was caused by the outbreak of the American Civil War in 1861. The United States was the world's largest producer and exporter of cotton. The Confederate states and major cotton producers implemented an "embargo" on their production, leading to a scarcity of this product in significant textile production markets such as England. This resulted in reduced working hours in factories and subsequently the dismissal of workers. (Narron & Morgan, 2015).

initiated thanks to various initiatives and events, especially with the support of the *Sociedade Madrépora*, mostly composed of Portuguese residents in Brazil.

The commission organised a competition to choose the draftsman and sculptor responsible for the statue of King Pedro V. Joaquim José Pirralho[8] was selected as the draftsman, while José Joaquim Teixeira Lopes[9] was appointed as the sculptor. The clay model was then transferred to plaster by António Almeida da Costa, owner of the Devesas Foundry in Vila Nova de Gaia.

The monument commission decided that the statue should be made in Portugal. Luís José Nunes, an expert goldsmith and the first director of the commission, was appointed to lead the project, which was initially intended to be carried out by the *Fundição do Arsenal do Exército* in Lisbon. However, due to financial constraints, this option could not materialize, leading to the decision to cast the statue in Porto. For this purpose, a plot of land on Rua Malmerendas[10] was provided free of charge by Mr. João Ferreira Dias Guimarães.

Between May and August 1863, a team of nine to twelve workers prepared the site for the casting. They built a large reverberatory furnace, a chimney or flue, and a walled pit to house the mould and carry out the casting of the statue, which would weigh around 100 *arrobas* (approximately 1,133.9 kg) (O Commercio do Porto, 1863).

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[8] Joaquim José Pirralho (1838 - 1882) was a painter, gilder, and bookbinder from Porto. He studied at the APBA between 1848 and 1858, where he was a disciple of the painter António Correia. Pirralho specialised in sacred painting and portraits, as well as bookbinding and lithography (Ferreira-Alves, 2008; M. M. Rodrigues, 1882; Sigarra -Universidade do Porto, 2017).

[9] José Joaquim Teixeira Lopes (1837-1918), a Portuguese sculptor and ceramist, studied at the APBA. After graduating, he dedicated himself to creating ceramic figurines depicting popular Portuguese scenes. His first large-scale sculpture, the monument to D. Pedro V in Porto, brought him recognition. He is considered one of the most important sculptors of the 19th century in Portugal (Ferreira-Alves, 2008; Teixeira Lopes Cruz, 2017).

[10] The land owned by Mr. João Ferreira Dias Guimarães was located between the current Rua Alves da Veiga, Rua Fernandes Tomás and Rua Duquesa de Bragança (now rua D. João IV) in Porto.

Copper, tin, and lead, materials essential for crafting the statue, were obtained through the supplier company *Pinto Leite & Irmãos*, based in London, United Kingdom.

For the casting of the piece, the goldsmith Nunes enlisted the assistance of workers from the nearby *Fundição do Bolhão* and a local bell founder[11]. The initial attempt, carried out in May 1864, proved unsuccessful due to a defect in the furnace, which caused severe damage to the casting box, destroying the chimney and the furnace. This resulted in a significant financial loss for the project. These events posed a major setback in the process, particularly given the lack of budget for a new attempt.

To repeat the casting process, additional funding was sought. Additionally, events were organised to raise funds, such as a bazaar at the Crystal Palace. Despite these efforts, the required amount could not be fully gathered. However, Luís José Nunes received a substantial donation from an anonymous benefactor, possibly Comendador Manuel Domingues Mariz, enabling them to proceed with the casting of the project.

For the second casting attempt, exhaustive precautions were taken to prevent another failure. The refurbishment of the foundry took six months, during which two furnaces were constructed instead of one. Despite safety measures being in place, just before melting the metal, the workers noticed that the floor under the furnaces was sinking. Anticipating another disaster, the workers and some members of the Commission joined forces to reinforce the ground beneath the furnaces.

On 16 September 1865, in coincidence with the anniversary of Pedro V's birth in 1837 and his coronation in 1855, the bronze casting of the statue was finally carried out. A few days later, the mould was destroyed, and it became evident that the piece had been cast impeccably. The statue of King Pedro V was inaugurated on 3 February 1866.

Upon completing the casting, the *Comissão dos Artistas do Monumento a D. Pedro V* dismantled the installation on Rua Malmerendas, marking the conclusion of this endeavour.

[11] Possibly, it refers to the bell foundry in *Pedras Rubras*, Maia, as mentioned in the *Inquérito Industrial* of 1881 (pages 43-44).

The remaining materials, such as the shed and tools, valued at 600,000 reis, were handed over to Mr. Luís José Nunes as a token of appreciation for his work as a founder and his tireless dedication. Additionally, the plaster version of the statue was donated to the *Sociedade Madrépora* in Rio de Janeiro as a gesture of recognition for their valuable contribution to the project.

1.4.4 20th Century: emergence of art foundries in Portugal

The emergence of art foundries in Portugal, much like in other countries, stemmed from the need for institutions that transcend industrial production. The intent was for these art foundries to serve as spaces where the training and expertise of the founder would provide the understanding and sensitivity required to address the challenges that arise in the final stage of the creative process of a bronze work of art.

Art Foundries in Vila Nova de Gaia

In response to this need, the establishment of *Adelino Sá Lemos Foundry* (ASLF) emerged as a timely and relevant answer to the expressed demand.

Sá Lemos acquired his expertise in artistic casting techniques during his training in Paris. He arrived in the city alongside his father-in-law, José Joaquim Teixeira Lopes, his brother-in-law[12], António, and the sculptor Joaquim Meireles (Leão, 2005; Pedrosa, 1981).

Adelino Sá Lemos set up his first foundry at his home on Rua Almeida da Costa in the Devezas area of Vila Nova de Gaia. It was there, in 1904, that the statue honouring Soares dos Reis, created by António Teixeira Lopes, was cast. In 1910, Sá Lemos obtained

[12] Adelino Sá Lemos was married with Emilia Teixeira Lopes.

permission from the City Council to build a new house and workshop at 1101 Avenida da República in Vila Nova de Gaia, previously known as Avenida Campos Henriques. The family moved there in 1919. In this larger space, Adelino Sá Lemos worked with his sons, José María and Fernando. Adriano Teixeira Lopes, Sá Lemos's brother-in-law, also participated, though he had a less active role in the foundry (Pedrosa, 1981).

According to the records in a catalogue published by themselves, ASLF became particularly well-known for casting bronze works by Teixeira Lopes and Soares dos Reis (Sá Lemos, 1920a). One of his notable clients was the *Academia Portuense de Belas Artes* (APBA), which, in 1912, commissioned the casting of the monumental statue of Conde Ferreira, now located in the Agramonte Cemetery (Padua, 1911). Later, between 1922 and 1927, the Escola de Belas Artes de Porto (EBAP) commissioned the foundry to produce a series of sculptures by Soares dos Reis (Escola de Belas Artes do Porto, 1927).

Within this series of commissions carried out by EBAP, notable works include the head of the statue of Conde Ferreira, the bust of Dr Correia de Barros, the bas-relief of Augusto Cândido Ramos, and the piece titled *Estudo Anatómico* (Escola de Belas Artes do Porto, 1927). These sculptures, along with others that do not bear the foundry's mark but may have been produced by the same entity, have been preserved at the MNSR since 1932. There is a possibility that some of these pieces reproduced by ASLF are the sculptures Busto de Firmino, O Pescador, S. José and S. Joaquim, which have been the subject of study in this project. However, in contrast to the examples mentioned earlier, these sculptures are not specifically cited in the documents preserved in the archive of the *Faculty of Fine Arts at the Universidade do Porto* (FBAUP).

In 1921, the foundry known as the *Empresa Artística Teixeira Lopes* (EATL) was established on Rua Veloso da Cruz, situated just a short distance from the residence of the renowned artist António Teixeira Lopes. The building of this foundry, which still stands today, was meticulously organised into different work areas. On the ground floor, there were offices and spaces designated for casting tasks, such as the reduction area, the actual foundry,

the chiselling area, as well as other auxiliary workspaces. In contrast, the upper floor housed spaces dedicated to modelling and perfecting the artworks.

Despite sharing family ties through affinity, it is important to highlight that the EATL had no connection with the ASLF. Indeed, these two companies experienced certain tensions on several occasions, mainly related to the acquisition of public sculptural projects. It is relevant to note that in these conflicts, despite sharing the surname, António Teixeira Lopes remained neutral, prioritising the strong family relationship he maintained with Adelino Sá Lemos (Pedrosa, 1981).

The original foundries of ASLF and EATL played a fundamental role in shaping the future owners of the foundries in Vila Nova de Gaia throughout the 20th and 21st centuries.

A clear example of this influence is the third foundry to emerge, *Bernardino – Fundição d'Arte*, established in 1933, which continues to operate to this day.

The current owner, Carlos Bernardino, recounts that this company originated in response to a growing demand for casting services. Bernardino Inácio, the founder of this company, likely gained experience in one of the two foundries during the end of his adolescence. As casting orders increased, Bernardino, along with two collaborators, rented additional space to carry out the casting process outside of regular working hours. It was in the year 1935 that Bernardino Inácio started his independent venture (C. Bernardino, personal communication, 8 January 2021).

From its foundation, the *Bernardino Inácio* foundry occupied the same workshop in the locality of Gulpilhares until 2023, the year in which it relocated its operations to the parish of Perosinho, Vila Nova de Gaia

A notable feature of this foundry is that few of its sculptures bear a casting mark, which has posed challenges in identifying the works produced by the company.

Within this broader context of the foundry's legacy, several craftsmen went on to establish their own workshops. Among them were two accomplished figures, José de Castro Guedes and António Maria Ribeiro, who began their careers at ASLF. In 1937, they jointly founded *Fundição de Arte Guedes e Ribeiro Lda*., establishing their workshop at 640 Rua Conselheiro Veloso da Cruz, a place formerly associated with EATL. This pivotal transition is meticulously chronicled in the company's catalogue, wherein Guedes and Ribeiro proudly affirm their proprietorship of the former ASLF and EATL. This historical connection is strategically emphasised in their promotional endeavours, capitalizing on the esteemed reputations of these two venerable establishments.

Nevertheless, in 1941, the partnership dissolved, with António Maria Ribeiro transferring his share to the wife and son of José Castro Guedes. In exchange, he retained ownership of the former ASL foundry, located at Av. Da República 1101 (Pedrosa, 1981).

In 1979, the Guedes & Ribeiro Foundry, still situated on the former EATL' building, underwent a change in ownership. It was acquired by José de Silva Abreu, who had commenced his training at this foundry at the age of nine (Pedrosa, 1981)**.** Subsequently, he continued his professional journey within the same company and, from 1966 onwards, worked as a finishing expert at the Bernardino Inácio Leite foundry, then owned by the founder's son (Leite, 1967).

This transaction resulted in a change in the company's name, becoming known as *Fundição José da Silva Abreu* (Pedrosa, 1981).

After the April 25, 1974, Revolution, several new art foundries emerged. Notably, *Fundição Araújo & Guedes* developed from the *Fundição José Silva Abreu*. The *Fundição Lage*, whose owner gained experience in José de Castro Guedes' family foundry, also came into existence. Additionally, there is the *Fundição do Regato* and the *Fundição Cosme e Filhos*, whose owner previously worked at Bernardino Inácio Leite's company (Leite, 1967). Among these, Bernardino Inácio, Lage, and Regato foundries are still operational today.

Art Foundries beyond Vila Nova de Gaia

In parallel with ASLF, there was also a foundry named *Fundição Venâncios* in Lisbon, owned by Venâncio Rodrigues Andrade França. Evidence of this company's existence dates back to 1912 when it crafted the bronze palm that now adorns the commemorative plaque at the former Democratic School Centre on Rua Campo de Ourique 93. This plaque serves as a reminder of the starting point of those who initiated a revolution the 4th October 1910. This later established the First Republic in Portugal (Ribeiro, 1915).

In 1917, the *Fundição Venâncios* cast the bronze sculpture *Filho Pródigo* (The Prodigal Son) by the sculptor Alberto Nunes. This was made possible through the Valmor legacy, from which payments had already begun three years earlier (Academia Real de Belas Artes de Lisboa, 1901; França, 1914).

Another notable sculpture cast by the Fundição Venâncios is the artwork titled *O Rapto de Ganimedes* (The Abduction of Ganymede), created by the sculptor António Fernandes de Sá in 1898 and subsequently cast on 18 October 1915. The sculpture, which bears the foundry's signature on the lower back of the figure, was originally situated in the Jardim da Cordoaria, in Porto; since 2025, however, it has been relocated to the Praça da República.

In Lisbon, the foundry of *Augusto d'Abreu*, later known as *Fundição Abreu e Filho*, was a prominent establishment in Portugal, renowned for its craftsmanship and specialisation in the lost-wax casting technique. This method, exclusively employed, allowed them to produce high-quality bronze artworks. The foundry worked closely with artists to ensure that each piece met the highest artistic and technical standards (Câmara Municipal de Oeiras, 2001).

The foundry, originally located on Estrada da Luz in Lisbon, was later relocated to Estrada do Desvio in Odivelas, where it initially set up a temporary structure, possibly to carry out the casting of the equestrian statue of King João IV, commissioned in 1941 to be installed in Vila Viçosa, Évora District (Câmara Municipal de Loures, 1941; Ministério das Obras

Públicas, Comércio e Industria, 1941). Although the exact date of its closure is unknown, it is documented that the foundry was still operating in Odivelas in 1954, as that year the Museu Nacional Soares dos Reis (MNSR) requested a quotation for casting the sculpture *História*, a proposal that was ultimately declined (Barata Feyo, 1954b).

This foundry played a key role in the official commissions during the 1940s and 1950s. It was responsible for producing the bronze sculptures displayed at the exhibition dedicated to Soares dos Reis, organised by the *Comissão dos Centenários* in 1940 at the MNSR (Comissão Executiva dos Centenários, 1940). Similarly, Diogo de Macedo, then director of the Museu Nacional de Arte Contemporânea (MNAC) in Lisbon, selected this foundry to reproduce *O Desterrado (The Exiled)* in bronze.

Further south, in Montemor-o-Novo, Évora, the *Fundição Mão de Fogo* operates to this day. Founded in the first years of the 21st century, the owner of the foundry, Rui Palmas, was trained in Art casting in the Basque Country.

1.5 FINAL REMARKS ON CHAPTER 1

The emergence of artistic bronze sculpture in the 19th century marked a significant milestone in the history of Portuguese foundry work. This period initiated a tradition that would gradually become embedded in the country's artistic and cultural sphere.

Although the 18th century had produced only one major example, namely the equestrian statue of King José I, the 19th century witnessed a rise in sculptural production. Despite the lack of dedicated art foundries, various works were cast in military or industrial facilities. These early undertakings, carried out under demanding conditions, became landmarks within their local contexts, bearing witness to the technical skill and dedication of the foundry workers involved.

In the 20th century, foundry work in Portugal underwent a significant transformation, adapting to both stylistic changes and technological innovations, particularly in Vila Nova de Gaia. This region became a centre of artistic production and the birthplace of prominent sculptors specialising in bronze. The development of foundry processes in Vila Nova de Gaia, from the early foundries of the 20th century to the present day, illustrates this evolution.

According to Carlos Bernardino (personal communication, 8 January 2021), owner of *Bernardino Fundição d'Arte*, the oldest still operating foundry in Portugal, early work in the field was particularly demanding. The foundry process was almost entirely manual, relying on locally available resources; coke coal fuelled the furnaces, while materials like silica sand were transported by ox-drawn carts from the nearby region of Miramar. The skills and expertise of workers were crucial, developed over long apprenticeships under difficult conditions, given the high temperatures and physical effort required in the manufacturing process.

The advent of electricity marked a pivotal transformation in Portuguese foundries, facilitating the use of machinery such as overhead cranes and ventilation systems. These innovations improved the handling of heavy materials and enhanced temperature control, significantly increasing efficiency and production capacity. Additionally, the evolution of fuel types, from coke coal to diesel, and later to a combination of diesel and oils, further optimised the foundry process.

This shift allowed for more efficient combustion, reducing mould firing times and accelerating bronze casting. Barinaga (1874) notes that in the late 19th century, mould curing could take two to three weeks, limited by the lower combustion efficiency of coke compared to modern fuels. In contrast, contemporary energy sources now reduce mould firing and drying to as little as 24 hours in some cases, exemplifying the drastic improvements in foundry technology over time.

In recent decades, the adoption of digital technologies and 3D modelling has expanded creative possibilities, allowing for the production of more complex and detailed pieces. The

use of rubber and silicone moulds has contributed to greater precision and efficiency within the process.

Political changes have also impacted the sector: before the Revolution of 24 April 1974, most commissions for statuary came from government ministries. Subsequently, local councils became important patrons, expanding demand. Today, Portuguese foundries attract commissions from national and international artists, valued for both quality and competitiveness.

Nonetheless, a decline in foundry labour has affected the transfer of specialised skills, as fewer young people are willing to commit years to learning a trade that does not offer high wages. Although the number of foundries has decreased, the sector has adapted to new forms of expression and technology, maintaining its international relevance.

CHAPTER 2. SOARES DOS REIS AND HIS TIME: ARTISTIC CONTEXTS, CREATIVE PROCESSES, AND TECHNICAL APPROACHES

2.1 INTRODUCTION

The main objective of this study is to conduct an in-depth analysis of the bronze sculptures cast from the original plaster works of António Soares dos Reis. However, it is essential to first establish a contextual framework that encompasses both the artist's life and work, as well as the creative and technical processes that defined his sculptural production.

Although bronze possesses remarkable physical and mechanical properties that make it an ideal material for sculpture, most of Soares dos Reis' works were not originally conceived for execution in this medium. Documentary and bibliographic sources indicate that only the bust of *Francisco de Almada e Mendonça*, the monumental statue of *King Afonso Henriques*, and a *medallion of Camões* were explicitly designed to be cast in bronze (Comissão do Monumento a D. Affonso Henriques, n.d.; Macedo, 1945). Notably, both the bust and the monumental statue were produced in this material during the artist's lifetime, enhancing their historical and technical relevance. A detailed study of these works not only provides insight into Soares dos Reis' engagement with bronze casting but also offers a broader

understanding of 19th-century sculptural practices and the technical evolution of foundries in Portugal.

To better understand these technical and material choices, it is necessary to first explore the biographical and artistic background of Soares dos Reis.

2.2 ANTÓNIO SOARES DOS REIS: LIFE AND WORK

Born on 14 October 1847 into a working-class family, Soares dos Reis demonstrated an innate artistic talent from an early age. His potential was recognised by painter Francisco José Resende[13] and merchant Diogo José de Macedo, whose family would later play a crucial role in preserving and safeguarding his artistic legacy (Macedo, 1945; Santos, 2009; Valle, 1981).

Soares dos Reis embarked on his artistic education at the APBA on 1 August 1861. His training there was rooted in a rigorous academic curriculum that encompassed disciplines essential to classical artistic education. These included drawing from prints and plaster models, life drawing, architecture, painting, anatomy, and perspective (Soares dos Reis, 1905). Among his principal instructors were T.M. de Almeida Furtado (drawing), José Carneiro, Joaquim de Costa Lima, and M. de Almeida Ribeiro (architecture and perspective), Manuel de Fonseca Pinto (sculpture), and António Corrêa (painting and anatomy) (Soares dos Reis, 1905).

According to Diogo de Macedo (1945) Soares dos Reis was also influenced by prominent portuguese artists such as Domingos Sequeira, Vieira Portuense, João Baptista Ribeiro, and Joaquim Rafael. His early works reflect the strong academic foundations instilled during his

[13] Francisco Resende was a professor of historical painting at the APBA (Comissão Executiva dos Centenários, 1940).

time at the APBA. Among these, two notable pieces stand out: *Figura Feminina* (Female Figure) (1865), currently housed at the FBAUP, and *Hercules Esmagando o Gigante Anteu* (Hercules Crushing the Giant Antaeus) (1866), a bas-relief preserved at the MNSR. The latter marks the culmination of his academic training at the APBA. His studies primarily explored themes of mythology and religion, central elements of 19th-century academic artistic education across Europe.

Upon completing his studies at the APBA in 1866, Soares dos Reis was awarded first prizes in drawing, architecture, and sculpture (Comissão Executiva dos Centenários, 1940). Following this achievement, he applied for a state-funded scholarship to pursue further studies abroad (M. Rodrigues, 1887a). These competitive scholarships, granted to outstanding graduates from the Fine Arts Academies of Porto and Lisbon, required applicants to demonstrate their proficiency through rigorous examinations. Soares dos Reis secured the scholarship with his sculpture *Bust of Firmino*. Both the original plaster model and its later bronze version form part of the MNSR collection.

His scholarship enabled him to continue his studies in Paris, where he arrived on 6 November 1867. He initially settled at 63 Rue de Seine and, after a brief waiting period, gained admission to the renowned École Impériale des Beaux-Arts. There, he studied under the guidance of François Jouffroy[14], a prominent academic sculptor known for his emphasis on

[14] François Jouffroy (1806-1882) is one of the most representative sculptors of 19th-century official French sculpture. His most renowned work is *Premier Secret Confié à Vénus***,** currently displayed at the Louvre Museum, which is a notable example of late Neoclassicism. Jouffroy also created a series of works in architectural settings and in both official and private collections. However, Jouffroy is one of the 19th-century sculptors who have faded from collective memory. According to Ferlier (2006), this is because the artist remained loyal to an ethereal classicist style during a period and artistic environment where Romanticism and Naturalism were beginning to dominate the art world. Jouffroy is particularly well-known and valued for his role as a teacher, influencing many students, some of whom became key figures in the sculptural avant-gardes of the 20th century (Ferlier, 2006).

classical forms and rigorous technical training (Baldaque & Pinto de Almeida, 1988; Macedo, 1945). As part of his academic preparation, Soares dos Reis also attended courses in Anatomy and Philosophy of Art, disciplines that further refined his sculptural approach.

Just over a year after joining Jouffroy's studio, Soares dos Reis was officially admitted to the *École des Beaux-Arts* in April 1869. Given the institution's preference for French students, competition for admission among international candidates was particularly intense (Macedo, 1945). To secure his place, he created the bust *Negro sobre Placa*, a piece that exemplifies a clear Neoclassical influence and reflects the technical evolution he underwent during his training in Paris under the guidance of Jouffroy (Baldaque & Pinto de Almeida, 1988).

While at the *École*, Jouffroy remained his mentor in sculpture. In addition to this tutelage, Soares dos Reis received training from other notable professors, such as M. Taine in the Philosophy of Art, M. Heuzey in History and Archaeology, and M. Yvon in Drawing (Soares dos Reis, 1905). Throughout his period in Paris, Soares dos Reis received several awards in the field of sculpture as an École student (Soares dos Reis, 1905).

The American sculptor Auguste Saint-Gaudens (1913), who studied alongside Soares dos Reis in Paris and later shared a workshop with him in Rome, describes him during his student years :

[...] was long, dark and thin, of an effeminate nature, inclined to melancholy, the kindest man in the world [...]

During his years in the French capital, Soares dos Reis produced several notable sculptures, including *Academia – Homem Sentado* (Academia – Seated Man) (1868), completed in Jouffroy's studio, and *O Pescador* (The Fisherman) (1870), created at the École des Beaux-Arts. Both artworks exist in plaster and bronze versions and have formed part of the MNSR collection since 1932, having been transferred from the EBAP.

Following the outbreak of the Franco-Prussian War in 1870, Soares dos Reis returned to Portugal. However, six months later, he travelled to Rome, arriving on 17 January 1871

(Macedo, 1945). Initially, he intended to further his training under the sculptor Giulio Monteverde, an artist associated with the Verismo movement, which shared many principles with French Naturalism (Beccaro, 2009). Despite these intentions, Soares dos Reis never collaborated with Monteverde nor enrolled in any art academy in Rome (Soares dos Reis, 1905).

During his Roman period, Soares dos Reis devoted himself to the creation of *O Desterrado*, regarded as one of his most significant works. However, his artistic aspirations were abruptly disrupted by financial constraints and institutional decisions that impacted his scholarship (Macedo, 1945).

In July 1872, his scholarship was suspended, forcing him to leave Rome before completing *O Desterrado*. Despite this setback, he returned to Portugal with preparatory pieces modelled from life, which allowed him to finalise the sculpture in his Porto workshop at Nº 99 Rua de Malmerendas[15] (Macedo, 1945; Soares dos Reis, 1905).

The workshop established by Soares dos Reis served a dual purpose: it functioned both as a practical space for artistic creation and as a social gathering point for artists and intellectuals. Unlike Lisbon**,** Porto lacked social meeting places similar to those in Paris, a concern frequently voiced by contemporary intellectuals (Serén & Pereira, 1994).

In this context, initiatives emerged that later materialised in the *Centro Artístico Portuense* (1880-1893)**,** located on Rua Moinho de Vento[16], with Soares dos Reis serving as its first president, and in the magazine *A Arte Portuguesa* (1882-1884) (Comissão Executiva dos Centenários, 1940; Macedo, 1945, 1989).

[15] Currently Rua Alves da Veiga in Porto, Portugal. Before its urbanistic growth, this area, which was part of the Santa Catarina hills, was a popular spot for families to have picnics during the summer. However, these gatherings were often disrupted by robberies or incidents of drunkenness by some attendees, which spoiled the outings (Basto, 1934).

[16] Currently Rua Sá Noronha in Porto.

In 1875, Soares dos Reis relocated his residence and workshop to No. 12, formerly Rua Nova da Serra do Pilar, in Vila Nova de Gaia[17], leaving behind his previous studio in Porto. From his new base, he remained actively engaged in the city's artistic and intellectual life. He cultivated relationships with local artists and intellectuals, and regularly participated in cultural debates and public exhibitions. His contributions included participation in the Triennial Exhibitions organised by the APBA in 1874, 1878, and 1881, as well as in the *Exposition Universelle* held in Paris in 1878 (Academia Portuense de Belas Artes, 1874, 1878, 1881; Santos, 1998).

In 1881, the EBAP separated from the APBA. Under this new institutional framework, Soares dos Reis, then a professor of sculpture at the EBAP, proposed a comprehensive reform of the artistic training system. The primary aim of this reform was to foster the development of students' talents, particularly those with outstanding artistic and technical skills, allowing them to progress based on merit rather than a rigid curriculum.

However, the *Conselho Superior de Instrução* rejected his proposal, arguing that it conflicted with the existing academic regulations**,** which remained unchanged in 1881 decree reorganising the Fine Arts Courses (Queiroga, 2011)**.** The original version of his reform proposal was published in issue No. 9 of the journal *A Arte Portuguesa*, edited by Manuel Rodrigues (1882). Frustrated by the rejection, Soares dos Reis even contemplated resigning from his teaching position at the EBAP (M. Rodrigues, 1887a).

Despite these challenges, Soares dos Reis continued to teach sculpture at the EBAP. In parallel, he also played a key role at the *Centro Artístico Portuense*, where he enjoyed significantly greater freedom to implement his own pedagogical approaches. Unlike the more rigid and academic structure of the Fine Arts Schools, the *Centro* fostered a flexible, practice-based model of artistic education (Comissão Executiva dos Centenários, 1940; Ribeiro, 1896).

[17] Currently Rua de Camões 33, Vila Nova de Gaia (Azevedo & Santos, 1881).

Despite his artistic accomplishments, Soares dos Reis struggled to gain widespread recognition as a sculptor. During the 1870s and 1880s, Portuguese sculptors faced significant challenges in securing commissions, as the art market was dominated by a bourgeois clientele with a preference for more conventional styles. This situation worsened with the increasing popularity of mass-produced decorative objects, such as bibelots, which, while making artwork more accessible to the middle class, reduced opportunities for sculptors working on unique, large-scale pieces (Matias, 1993).

At the time, official taste dictated the artistic trends of Portuguese society, limiting the creative freedom of sculptors. Many private patrons preferred idealised, academic styles**,** which often clashed with Soares dos Reis' inclination toward Realism. This preference may have contributed to the rejection of some of his works, including the busts of *Ms. Elisa Leech* and *Joaquim Pinto Leite*, which failed to align with prevailing artistic expectations (Arroio, 1899; Matias, 1993).

Over the course of his career, Soares dos Reis supported himself primarily through private commissions, sculpting busts of prominent figures, allegorical works, and sculptures that were later executed in stone by stonemasons or reproduced in ceramics. Although he participated in several public projects for monuments, many of these commissions did not materialise. Among his notable completed works are the statue of *Conde de Ferreira* (1876), the bust of *Francisco de Almada e Mendonça* (1883), the statue of *Avelar Brotero* (1886), and the monument to *King Afonso Henriques* (1887) (Baldaque & Pinto de Almeida, 1988).

Despite securing prestigious commissions and even contributing financially to the establishment of a school prize using his own personal resources, Soares dos Reis experienced persistent financial hardship (Macedo, 1945). To supplement his income, he worked on illustrations and engravings for publications, though the fees were often minimal or, in some cases, non-existent. In a personal account of his career, he acknowledged this financial hardship, stating:

“No aponto outros trabalhos porque, ou tenho recebido por eles uma simples remuneração, ou tenho-os feito grátis” (Soares dos Reis, 1905).

"I do not list other works because either I have received only a modest compensation for them, or I have done them for free."

In his final years, the combination of economic hardship, unfulfilled commissions, and personal difficulties took a toll on his health and well-being (De Sousa Vieira, 1923). His declining health contributed to delays in significant projects, most notably the monumental statue of *King Afonso Henriques*, which was completed and inaugurated in 1887 (Soares dos Reis, 1885a). During this period, he became increasingly withdrawn, distancing himself from colleagues who, as noted by De Sousa Vieira (1923), struggled to understand his fluctuating moods and growing frustration. Despite this, he maintained close ties with a small circle of confidants and sought temporary relief outside Porto and Vila Nova de Gaia, attempting to manage both his physical ailments and psychological distress (Comissão Executiva dos Centenários, 1940; Macedo, 1989).

Soares dos Reis was often described as a man of great sensitivity and kindness, but also as someone prone to melancholy and moments of irritability. The teacher and art critic António Arroio (1899) noted that the sculptor possessed a gentle yet troubled nature. This emotional disposition was also noted by his contemporaries. For instance, Saint-Gaudens (1913) reflected on the deep sadness expressed in *O Desterrado*, stating:

"Its melancholy was in complete accord with Soares' own nature."

Some scholars, such as Germano de Sousa Vieira (1923), suggest that this emotional fragility may have contributed to his tragic death. On 16 February 1889, at the age of 41, Soares dos Reis took his own life in his home-studio in Vila Nova de Gaia. Just one day earlier, he had attended a meeting at Café Suíço with colleagues from the *Comissão Executiva do Monumento ao Infante D. Henrique*, demonstrating his ongoing commitment to artistic projects (Comissão Executiva dos Centenários, 1940; Macedo, 1989).

His death left his wife, D. Amélia Aguiar de Macedo, widowed and his children, Raquel and Fernando, orphaned. The personal tragedy of his passing deeply affected those closest to him, yet it also marked a turning point in the recognition of his artistic contribution. In the years that followed, exhibitions, publications, and institutional tributes gradually helped to shape the perception of his work. His enduring artistic legacy not only shaped subsequent generations of Portuguese sculptors but also affirmed his role as a central figure in the development of 19th-century European sculpture.

2.3 THE CREATIVE AND TECHNICAL PROCESS OF SCULPTURE

Understanding the technical foundations of Soares dos Reis' sculptural production requires a closer examination of the historical methodologies that shaped his practice.

Sculpture, as an artistic discipline, has demonstrated a remarkable continuity in its technical processes throughout history, undergoing relatively few fundamental modifications over the centuries. While the artistic field has undergone numerous transformations, traditional sculptural techniques have retained their core principles, adapting selectively rather than being replaced by avant-garde movements or new materials (Sauras, 2003).This persistence suggests not only the technical resilience of these methodologies but also their functional efficacy, reinforcing their relevance in contemporary sculptural practice.

The sustained use of classical sculptural techniques, while not excluding the assimilation of modern innovations, attests to both the technical mastery of sculptors and the practical advantages of these methods. Their longevity underscores their enduring pedagogical value, as evidenced by their continued presence in the academic curricula of leading institutions dedicated to Fine Arts education. A pertinent example is the FBAUP, the alma mater of Soares dos Reis, where traditional sculptural techniques such as stone carving, clay

modelling, and plaster casting remain fundamental components of artistic training (Ferro, 2005; Moutinho, 2015; A. Rodrigues, 2020).

Leon Battista Alberti, in *De Statua*, published in 1451, describes various sculptural approaches based on the material and technique employed. His classification remains relevant in understanding the work of Soares dos Reis, who engaged in two principal methodologies. The first corresponds to what the Greeks referred to as *plasticous* and the Renaissance termed *fictores*, referring to artists who shape and manipulate the material through both additive and subtractive processes, forming the sculpture by adding and removing material. Moreover, Soares dos Reis also adopted the subtractive approach characteristic of stone carving, in which the sculptor is exclusively dedicated to removing excess material to reveal the intrinsic form concealed within the marble block. Alberti explicitly categorises this method as sculpture in its purest form, reserving the term *sculptores* for those who work exclusively through this process (Alberti, 1999).

The production of a bronze sculpture, unlike stone carving, unfolds in two distinct phases. The first stage encompasses the conception and materialisation of the artwork through the modelling technique, typically in clay or wax, followed by the creation of a plaster mould. This process demands a combination of artistic creativity and technical precision on the part of the sculptor, as it involves not only defining the features and formal characteristics of the piece but also anticipating the transformations it will undergo during the casting process. Depending on the methodology employed, some sculptors personally undertake the mould-making process to reproduce the model in plaster, while others collaborate with specialised mould-makers to refine the preparatory model and ensure its technical viability in the subsequent stages of the sculpture-making process.

The second phase is managed by the foundry, which undertakes the preparation of the mould and the subsequent bronze casting, a process that requires a high degree of technical expertise. This stage involves specialised techniques for creating the mould using the lost-wax or sand method, followed by the pouring of molten bronze and the finishing processes,

such as chasing and patination, which enhance the details and surface finish intended by the artist.

While this division of labour delegates significant responsibilities to the founder, the sculptor does not completely disengage from the process. In many cases, they closely oversee key moments, such as the bronze pouring, to ensure that the final sculpture faithfully embodies their original artistic vision.

Recent studies on the intersection between traditional and contemporary sculptural methodologies highlight the evolving relationship between manual craftsmanship and digital fabrication techniques. The integration of digital techniques such as 3D scanning and 3D printing into sculptural practice has expanded the possibilities for both the conceptualisation and materialisation of works (Alrashidi et al., 2024; S. Liu, 2024; Sargentis et al., 2022; Vasiljević et al., 2021).

This convergence underscores the continued relevance of historical sculptural techniques, not as immutable remnants of the past, but as adaptable frameworks that evolve alongside contemporary technological advancements, ensuring their enduring impact on artistic production.

2.4 ARTISTIC METHODOLOGIES AND TECHNICAL PRACTICES IN THE WORK OF SOARES DOS REIS

Building on the preceding discussion of sculptural methodologies, this section focuses on the specific creative and technical processes adopted by Soares dos Reis. His practice not only reflects the academic traditions of 19th-century sculpture but also reveals a personal adaptation of those conventions, which helped define his artistic identity.

Understanding these processes requires an interdisciplinary perspective that integrates historical analysis and technical examination. Soares dos Reis's artistic practice serves not merely as testimony to the endurance of classical sculptural principles, but as evidence of how such principles were reinterpreted and innovatively applied within the Portuguese context.

This reliance on classical knowledge had deep roots in Portuguese sculptural education, as seen in the writings of Joaquim Machado de Castro, renowned for creating the monument to King José I in Lisbon. In his *Dicionário de Escultura*, published in 1788, Machado de Castro emphasised the relevance of various fields of knowledge essential for sculptural training. These included geometry, external anatomy and physiognomy, as well as an understanding of sacred, ecclesiastical, profane, and mythological history (Machado de Castro, 1937).

Beyond this formal academic foundation, Soares dos Reis's creative process followed a structured progression, beginning with preliminary sketches, followed by small-scale clay models, and culminating in the final sculpture in marble, wood, or plaster. While this workflow aligns with broader sculptural conventions of the 19th century, he introduced distinctive refinements, particularly in his exploration of form, volume, and texture. These elements allowed him to stand out in the artistic landscape of his time and to establish himself as a key figure in the history of Portuguese sculpture.

2.4.1 The Creative Process: From Concept to Execution

The artistic production of Soares dos Reis was predominantly the result of commissions, requiring a structured and highly methodical approach. His creative process followed a distinctive sequence of stages, beginning with preliminary sketches, progressing through small-scale clay models, and culminating in the final execution of the sculpture in marble, wood, or plaster (Santos, 1998).

This structured methodology is evident in notable works such as the bronze representations of *King Afonso Henriques* and the marble statue of *Avelar Brotero*, which illustrate the meticulous planning and technical precision that characterised Soares dos Reis's sculptural practice. His systematic approach ensured a balance between artistic expression and technical feasibility, allowing him to refine the composition, anatomical accuracy, and structural stability of each piece before its final materialization.

While his workflow aligned with broader European sculptural conventions of the 19th century, Soares dos Reis introduced distinctive refinements, particularly in his exploration of form, volume, and texture. His method involved careful attention to surface detail and material adaptation, reinforcing his ability to transition seamlessly between different media. This ability to integrate traditional academic techniques with a personal artistic sensibility positioned him as a key figure in the Portuguese sculptural landscape of his time.

Beyond the technical aspects of his sculptural method, curator Paula Santos (1998) highlights that the preparatory materials preserved at the MNSR reveal a recurring thematic focus in his work, with mythology, religion, and allegory playing a central role. These themes, reflecting his academic training and artistic influences, remained consistent throughout his career, shaping both his commissioned works and independent artistic explorations. The preparatory studies and objects he left behind demonstrate his meticulous approach to conceptualising sculptures, highlighting his deep engagement with historical and symbolic representation.

Arroio (1899) further distinguishes two primary approaches in Soares dos Reis's work. On the one hand, he produced sculptures based on the direct study of a model, adhering to strict realism and capturing precise anatomical details. On the other hand, he created works entirely from imagination, reflecting a stronger influence of his classical aesthetic training. Rather than a contradiction, this duality reveals the complementarity between academic rigour and creative freedom in his sculptural production.

In addition to traditional sculptural methods, Soares dos Reis's creative process sometimes involved collaboration with specialised artisans, who purchased his creations to reproduce

them in different materials. For plaster works, he sold his pieces to institutions such as the *Fábrica de Cerâmica de João dos Rios*, where they were reproduced in ceramic (Soares dos Reis, 1905).

Similarly, stonemasons, including *José Amatucci*, *Laurentino José da Silva and António Moreira Rato*, collaborated with the artist or acquired his models to translate them into stone sculptures, often intended for cemeteries or architectural embellishments (Moreira Rato, 1933; Queiroz, 2010; M. Rodrigues, 1887a). A notable example of this collaborative process is the sculptures of S. José and S. Joaquim, originally created for the *Capela dos Pestana* in Porto (Comissão Executiva dos Centenários, 1940). These partnerships highlight the complex network of artists, craftsmen, and institutions involved in 19th-century sculptural production in Portugal.

Although direct documentation on his technical procedures is limited, his surviving sketches and clay models provide valuable insights into his methodology. These preparatory materials illustrate the evolution of his artistic vision and highlight his meticulous approach to sculptural development. Additionally, references from contemporaries, including students and collaborators, offer further context regarding his working techniques.

2.4.2 The Role of the Sketch in the Creative Process

The sketch played a fundamental role in Soares dos Reis's preparatory work, serving not only as a means of visualising his initial ideas but also as a tool for refining form, structure, and composition. Unlike finished drawings intended for exhibition, these preliminary sketches were primarily concerned with conceptual planning and spatial arrangement rather than formal precision. While Soares dos Reis was a skilled draughtsman, his drawings for sculpture focused on anatomical structure, pose, and balance, rather than on aesthetic polish. The effectiveness of his sculptural work relied more on the clarity and purpose of these graphic studies than on the refinement of the drawings themselves.

Soares dos Reis used crayons and pens to produce quick, dynamic strokes, capturing the energy and rhythm of his compositions (Arroio, 1899). His sketches were not static representations but evolving studies, often undergoing multiple modifications and adjustments. This iterative process is particularly evident in his preparatory studies for works such as *Avelar Brotero* and *King Afonso Henriques*, in which successive versions reveal significant alterations in posture, gesture, and drapery. The final compositions resulted from a balance between realistic anatomical depiction and aesthetic idealisation, demonstrating the sculptor's mastery in conceptual development.

At this early stage, the artist frequently conducted anatomical studies based on live models, carefully analysing not only bodily proportions but also the natural flow of garments and their interaction with movement. These sketches were subject to multiple modifications, sometimes leading to drastic alterations in the final design. According to Arroio (1899), this iterative process is particularly evident in the preliminary studies for the statues of *Avelar Brotero* and *King Afonso Henriques*, both of which underwent significant compositional adjustments before reaching their definitive forms. The original sketches for these works, preserved at the MNSR and published in *Revista Mvsev* and *O Tripeiro*, reveal successive revisions that demonstrate the sculptor's meticulous approach to form and posture (Macedo, 1943; Pereira Dias, 1944; Santos, 1998).

In the case of *Avelar Brotero*, Soares dos Reis initially conceived the statue as a vertical composition with the figure standing, as seen in an early sketch published in *Mvsev* (Fig. 2.1), a decision later revised to achieve better spatial integration with its intended location (Pereira Dias, 1944). Similarly, the sketches for *King Afonso Henriques* exhibit notable modifications in posture and sword placement (Fig. 2.2 and 2.3), suggesting an evolving conceptualization of the figure's historical and symbolic representation (Macedo, 1943). Some of these preliminary studies have been preserved thanks to the efforts of Soares dos Reis's assistants and disciples, particularly Serafim das Neves, who played a key role in safeguarding the artist's preparatory materials.



Fig. 2.1



Fig. 2.2



Fig. 2.3

Fig. 2.1 - Preparatory sketches for the monument to Avelar Brotero (Coimbra). They reveal Soares dos Reis's initial intention to depict the figure standing. *Image published in Mvsev, Vol. III, No. 6, June 1944.*

Fig. 2.2 - Early sketches of the statue of King Afonso Henriques. The monarch is shown wearing a short tunic and holding a sword pointing downward. *Image published in Mvsev, Vol. II, No. 4, June 1943.*

Fig. 2.3 - Advanced sketch of the statue of King Afonso Henriques. The figure already wears the long tunic seen in the final version, although the sword still points downward and the shield remains raised. *Image published in Mvsev, Vol. II, No. 4, June 1943.*

Although Soares dos Reis frequently worked with live models, he sometimes relied on paintings, prints, and other sculptures as reference materials, particularly when depicting historical figures. This method of copying from plaster casts and prints was a fundamental part of academic training at the APBA, a practice that continued after its transition to the EBAP and was also implemented in the *Centro Artístico Portuense* (Soares dos Reis, 1905; Machado, 1947; Moncóvio, 2015). Soares dos Reis, having been both a student and later a professor in these institutions, mastered this approach, which is evident in his bust of

Francisco de Almada e Mendonça, for which he adapted features from a painting held by the Câmara Municipal do Porto (M. Rodrigues, 1885a; Soares & Lima, 1947). Similarly, when sculpting the head of *Avelar Brotero*, he referenced engravings of the botanist from the Universidade de Coimbra (Pereira Dias, 1944).

Beyond two-dimensional references, Soares dos Reis also produced studio sculptures that could serve as models for future works. *Figura Feminina* (Fig. 2.4a), created in 1866, during his formative years at the APBA, exemplifies this practice. The sculpture was conceived to allow variations in the positioning of the right arm and left hand, enabling the artist to experiment with different configurations. While not a preparatory sketch itself, it may have been used as a reference for later graphic or sculptural studies. The formal similarities between *Figura Feminina* and *Saudade* (Fig. 2.4b) suggest that works of this kind played a supportive role in his artistic process, offering adaptable sources for compositional or anatomical exploration (Macedo, 1945).



Fig. 2.4 - a) *Figura Feminina* (FBAUP), a studio sculpture from Soares dos Reis's formative years at the APBA. The separate right arm and left hand could be repositioned to explore different configurations, likely serving as a reference for later studies. b) *Saudade* (MNSR), a work that shares formal similarities with *Figura Feminina*, particularly in the pose, suggesting the use of studio pieces as adaptable creative resources.

Macedo (1945) also notes that Soares dos Reis often sculpted nude figures before draping them with wet cloths (*panejamentos*) to observe the natural fall of fabric over the body. This classical method, rooted in academic training, enabled him to achieve a high degree of realism in the depiction of drapery, as seen in several of his finished works. While the sketch itself could not capture the full effect of fabric in motion, it was instrumental in establishing the gesture and structure of the figure prior to such studies.

His drawing practice also informed his handling of clay, especially in establishing gesture and pose. While sketches were not finalised works in themselves, they served as graphic foundations that guided later modelling stages. This fluid progression from drawing to modelling reflects his ability to translate visual concepts into three-dimensional form, reinforcing the technical and artistic coherence that defined his creative method.

2.4.3 Preparatory Models

After defining the desired expressions and compositional structure through sketches, Soares dos Reis proceeded to create small-scale clay models, which served as an essential step in translating his ideas into three dimensions. These preparatory models allowed the artist to evaluate volume, proportions, and spatial relationships, offering an early visualisation of how the final sculpture would take form. By working in three dimensions at this stage, he could refine shapes, projections, and indentations, ensuring both aesthetic balance and structural feasibility. Additionally, this process enabled him to correct potential anatomical distortions or compositional imbalances, guaranteeing the physical stability of the final piece.

The use of preparatory models in sculpture became particularly widespread from the 15th century onwards, especially in Florence, which became a centre for their development. During the Renaissance, sculptors increasingly relied on clay models to refine their compositions before executing works in marble or bronze. In other European regions,

however, it remained common to work directly from drawings produced by architects, painters, or draftsmen, rather than from three-dimensional models (Wittkower, 2002).

By the 19th century, as sculptural practice evolved and academic institutions formalised artistic training, the use of preparatory models became an essential step in the creative process, allowing for greater precision in composition, anatomical accuracy, and material planning. During this period, these models were fully integrated into academic sculptural methodology, as exemplified in the work of Soares dos Reis.

Beyond their function as internal studies, these models also played a role in the professional practice of sculptors. They served as presentation pieces for clients, allowing commissioners to visualise the proposed work before its full execution. This practice was particularly important in the 19th-century context, as large-scale sculptures often required approval and financial investment prior to completion (Wittkower, 2002). Today, preparatory models are invaluable historical documents that offer insight into an artist's original intentions, working methods, and creative problem-solving strategies.

Models created by sculptors are typically small in scale due to their function as preliminary studies. Clay is often the preferred material because of its versatility, low cost, and ease of manipulation. However, some sculptors also experimented with wax and, in later periods, materials such as cardboard and plastics (Farag, 2020; Gramtorp et al., 2015; MacLagan, 1924; Miller, 2013; Poggi, 2012). While contemporary artists have diversified the use of materials in preparatory modelling, their primary role in refining compositional structure and volumetric relationships prior to final execution has remained unchanged.

A significant number of preparatory models by Soares dos Reis have been preserved, many of which were donated and are now exhibited at the MNSR and the Casa Museu Teixeira Lopes (Lacerda & Valente, 1943).

According to Arroio (1939), the remarkable state of conservation of these pieces is due to the fact that Soares dos Reis himself had them fired in one of the ceramic foundries in Vila Nova de Gaia, a practice that ensured their durability and longevity. This deliberate action

reflects a conscious effort to preserve his working studies, a decision that has allowed later scholars to examine his sculptural techniques in greater detail.

In addition to his clay preparatory models, bronze reproductions of these pieces were produced by the Teixeira Lopes foundry. These bronze versions, which were cast posthumously, are now distributed among various institutions, including the MNSR, the Casa Museu Teixeira Lopes in Vila Nova de Gaia, the Casa Museu of the Dionísio Pinheiro e Alice Cardoso Pinheiro Foundation in Águeda, and the Alberto Sampaio Museum in Guimarães. Several bronze models, cast through the Fundo João Chagas, are also preserved at the MNSR (Barata Feyo & Van Zeller, 1960).

2.4.4 Clay Modelling Stage

After completing the preparatory model, the final clay model is created, typically at a larger scale. This stage allowed the artist to refine details, proportions, and the overall composition before the sculpture was transferred to its final material. Importantly, the scale of the clay model did not always correspond directly to the finished work, as adjustments in size were often required depending on the intended medium. Sculptors could enlarge or reduce the model according to the specific demands of the final execution, particularly when transitioning from clay to bronze or stone.

At this stage, Soares dos Reis showed a strong preference for working with live models, a practice that, according to Diogo de Macedo (1945), enabled him to capture both the physical accuracy and emotional depth of his subjects. However, in cases where a model was unavailable, such as when sculpting historical figures or deceased individuals, he relied on photographic references. This was the case with the monumental statue of *Conde de Ferreira* and the busts of *Fontes Pereira de Melo*, *Emília das Neves*, and the Englishwoman *Elisa Leech*. Although photography provided a practical alternative, Soares dos Reis considered it a less ideal method compared to direct observation.

The creation of a stable framework is essential for supporting the weight and structure of the clay model. Traditionally, sculptors use wires, mesh, rods, and wood to construct internal armatures that prevented deformation during the modelling process. Although modern materials such as polystyrene and synthetic resins have been introduced, the fundamental principles remain unchanged.

For his clay models, Soares dos Reis used clay sourced from the pottery factories of Vila Nova de Gaia, as mentioned in his autobiography (Soares dos Reis, 1905). In addition to clay, sculptors employ a variety of tools to manipulate the material and achieve the desired level of detail. These include fine wire tools for hollowing and shaping the clay, wrapped wire tools for joining surfaces, and wooden-bladed tools, often made of boxwood, for smoothing and defining contours. Some tools combine wire and wood elements, offering greater versatility in sculptural modelling (Slobodkin, 1973).

Maintaining the moisture of clay is a fundamental aspect of the modelling process. Water is used to preserve the material's malleability, while damp cloths, or their modern equivalent, plastic coverings, prevent premature drying when the sculpture is not being actively worked on.

Despite its significance in sculptural development, the clay model is not intended as a final medium. Due to the fragility and ephemeral nature of raw clay, these models serve a transitional function, acting as the basis for the creation of plaster moulds, from which the sculpture is reproduced in more durable materials such as bronze, marble, or stone.

2.4.5 Plaster moulding stage

Once the clay sculpture reaches the desired form, a plaster mould is created, serving as a negative impression of the original clay model. This mould-making process is essential to ensure that the final material, also plaster in the case of Soares dos Reis' works, faithfully

replicates all surface details and sculptural recesses. To achieve the necessary precision, sculptors apply a fluid layer of plaster, allowing it to penetrate all areas of the clay model before adding subsequent, thicker layers to reinforce the structure.

A common technique among sculptors and mould-makers is to colour the first layer of plaster. This method facilitates the demoulding process by distinguishing between layers, preventing the loss of fine details during the extraction of the final cast. Traditional mould-making methods involve reinforcing the plaster with sisal and wood to create solid moulds. In contrast, contemporary sculptors use silicones and elastomers, which provide greater flexibility and allow for multiple reproductions with minimal alteration (Getsy, 2021).

Traces of the plaster moulding process can be observed in several of Soares dos Reis' surviving plaster models, where marks from his original working process are still identifiable. On some of these models, fingerprint impressions, spatula marks, and imprints left by dampened cloths remain visible, revealing the artist's direct interaction with the material (Murta et al., 2021).

Additionally, cutting tool marks and traces of dividing blades used to section the clay sculpture further highlight the technical aspects of his creative method. In certain cases, such as the *Busto de Negro*, *S. José*, and *S. Joaquim*, small holes and cross-shaped marks can also be observed. These are made using pantographs and compasses, essential tools for the precise scaling and reproduction of sculptures.

The creation and preservation of plaster moulds play a fundamental role in both protecting original artworks and producing replicas, particularly in cases where sculptures are intended for public spaces or commercial distribution. In Portugal, artists trained at institutions such as the FBAUP continue to receive instruction in mould-making techniques as part of their academic curriculum (Ferro, 2005, 2007).

While some sculptors make their own moulds, this task is often delegated to specialised mould makers or modellers, who ensure precise reproduction. In the field of casting, Portuguese foundries also employ the *formador* (mould-maker), responsible not only for

producing plaster figures but also for scaling them according to the artist's specifications (Moutinho, 2015; A. Rodrigues, 2020).

In the case of Soares dos Reis, he collaborated with assistants such as Marques Guimarães and Serafim das Neves, who were responsible for executing the moulds used in his sculptural process (Arroio, 1899; Macedo, 1945).

The resulting plaster models serve multiple functions: they allow clients to visualise the final sculpture before its execution in marble or bronze, and they also gain value as artistic objects in their own right. From the late 19th century onwards, plaster models came to be recognised as independent works of art, a trend evident in the work of sculptors such as Canova and Rodin, whose plaster pieces continue to be preserved and exhibited (Janson, 1985).

In the sculptural production of Soares dos Reis, plaster models not only provided a tangible record of his creative process but also played a crucial role in the preservation and reproduction of his works. The conservation of these models has ensured the survival of some of his sculptures, either in their original plaster form or through later reproductions in more durable materials such as bronze.

A representative case is the bronze bust of *Francisco de Almada e Mendonça*, whose original plaster model has been lost. To facilitate its recovery, the Comissão Executiva dos Centenários commissioned the creation of a plaster mould in 1940, from which a new version in the same material was produced (Comissão Executiva dos Centenários, 1940).

Similarly, the model of the statue of King Afonso Henriques played a key role in the dissemination and materialisation of the sculptor's work. As part of the commemorative exhibition dedicated to Soares dos Reis in 1940, the considered original plaster mould was used to produce a new plaster model (Comissão Executiva dos Centenários, 1940). This model, in turn, enabled the creation of the final mould for the bronze casting of the statue, which is now located in the Castelo de S. Jorge, in Lisbon (Lopes, 1946).

These cases highlight the significance of plaster models not only as technical tools within the sculptural process but also as essential intermediaries in the preservation, reproduction, and dissemination of Soares dos Reis's work within the context of 20th-century Portuguese sculpture.

2.5 CREATIVE PROCESSES OF SOARES DOS REIS' CONTEMPORARIES

2.5.1 António Teixeira Lopes

António Teixeira Lopes (1866–1942) was a disciple of Soares dos Reis at the EBAP. As recounted in his autobiography *Ao Correr da Pena. Memórias de uma Vida...* (1968), their relationship was not particularly close. Despite being recognised for his talent as a student, Teixeira Lopes noted that Soares dos Reis appeared to favour another sculptor, Tomás Costa. Nonetheless, this did not diminish his admiration for his former teacher, particularly his skill as a modeller. He did, however, express reservations about Soares dos Reis' marble works, which he viewed as overly refined and heavily influenced by the Italian style.

Teixeira Lopes provided detailed accounts of his own creative and technical processes through personal writings and public statements. His creative methodology displays several parallels with that of Soares dos Reis, particularly in the use of preparatory drawings, clay modelling, and the production of plaster moulds as intermediary stages. A clear illustration of Teixeira Lopes' technical approach is the set of monumental bronze doors created for the Church of the Candelária in Rio de Janeiro. The project began with detailed drawings and was followed by clay modelling in his workshop. Once modelled, the doors were cast in plaster in sections and then sent to the Parisian foundry of *Edmond Capitain and Hyacinthe*

Salin for bronze casting (T. Lapa & Fontão, 2000). As Teixeira Lopes remained in Vila Nova de Gaia, supervision of the casting was delegated to his brother, José Teixeira Lopes.

Throughout his career, Teixeira Lopes made extensive use of live models, documenting not only their physical features but also aspects of their personality and background. This attention to detail reveals a desire to imbue his works with both technical rigour and expressive character. He also maintained a close relationship with the press, often inviting journalists to his studio to publicise ongoing projects, particularly large-scale commissions.

The *École des Beaux-Arts* played a fundamental role in the artistic training of Teixeira Lopes, just as it did for Soares dos Reis and other sculptors of the period. The academic environment provided rigorous instruction in drawing, anatomy, and classical composition, aspects that profoundly influenced his sculptural approach. His time in Paris and his engagement with the *Salon* significantly shaped his professional trajectory, reinforcing the structured process he applied in his work.

His experiences in Paris played a central role in shaping his professional outlook. While studying and exhibiting in the French capital, he gained first-hand knowledge of the artistic dynamics surrounding the Salon de Paris. Although he acknowledged the Salon's value as a platform for recognition, he also expressed criticism of its tendency to promote repetition and conformity. According to his writings, original ideas presented in one edition of the Salon were often imitated in subsequent ones, a practice he viewed as detrimental to artistic authenticity.

Upon returning to Portugal, Teixeira Lopes encountered a very different scenario. He lamented the lack of institutional support for artists, the undervaluation of sculpture in public commissions, and the frequent imposition of changes to his designs by bureaucratic entities. Despite these challenges, he succeeded in establishing a prolific studio in Vila Nova de Gaia and developed a sustainable artistic career that spanned several decades. His studio became a dynamic centre for sculptural production and innovation.

Unlike Soares dos Reis, whose career was prematurely cut short, Teixeira Lopes enjoyed a long and prolific trajectory, which enabled him to explore a wider range of sculptural techniques and materials. While both artists demonstrated exceptional skill in marble carving, Teixeira Lopes produced a significantly greater number of works intended for bronze casting, a medium that gained increasing prominence in public commissions during the late 19th and early 20th centuries.

His use of foundries was not limited to Paris; he also played a central role in developing Portugal's national artistic foundry sector, helping to reduce the country's reliance on foreign workshops. This vision, shared with his father Joaquim Teixeira Lopes and his brother-in-law Adelino Sá Lemos, led to the creation and growth of the *Empresa Artística Teixeira Lopes* and the *Sá Lemos foundry*. As a result of this initiative, public institutions in Portugal began to place increasing confidence in national foundries, which contributed to a local surge in bronze sculpture production.

2.5.2 Augustus Saint-Gaudens

Augustus Saint-Gaudens (1848–1907) was an American naturalist sculptor renowned for his role in the *American Renaissance Movement*[18]. His monumental works, particularly those related to the Civil War, remain highly esteemed in the United States.

In his autobiography, Saint-Gaudens expressed deep admiration for Soares dos Reis (Saint-Gaudens, 1913). The two sculptors shared both a personal and professional connection, having studied together in Jouffroy's studio and later at the École Impériale des Beaux-Arts

[18] The American Renaissance (1876–1917) was an artistic movement in the United States that sought to connect its cultural identity with the classical European legacy. Through murals, public buildings, sculptures, and other forms of artistic expression, the American Renaissance reflected values such as justice and freedom, while promoting a narrative of national pride and cultural grandeur (Moore, 1990).

in Paris. In 1868, Saint-Gaudens entered the school upon Jouffroy's recommendation, shortly after Soares dos Reis's admission. Following their time in Paris, they reunited in Rome, where they shared a studio in the gardens of the Palazzo Barberini. While Soares dos Reis was working on *O Desterrado*, Saint-Gaudens was engaged with *Hiawatha* (Greenthal, 1985). This shared artistic context, and the parallel development of these works suggest technical and thematic affinities between their respective practices (Tolles, 2021).

The École des Beaux-Arts was instrumental in shaping the creative processes of both artists, providing a rigorous academic framework based on drawing from life, classical sculpture, anatomy, and composition. Their methodologies exhibited strong similarities: both sculptors began their projects with drawings and annotated sketches, followed by clay models at various scales to refine pose, proportion, and composition.

Both artists also employed the study of drapery through real fabric, a technique often used to observe the natural fall and flow of cloth on the body. Saint-Gaudens applied this method in works such as the *Phillips Brooks Monument* in Boston, where he poured plaster over fabric to achieve realistic effects (Greenthal, 1985), a strategy closely aligned with that of Soares dos Reis.

Like his Portuguese counterpart, Saint-Gaudens frequently produced multiple clay models of a given work before selecting the definitive version. This approach is particularly evident in major commissions such as the *Shaw Memorial* and the *Sherman Monument*, for which the final bronze versions were preceded by numerous studies and scaled prototypes (Greenthal, 1985).

Despite these methodological parallels, significant differences marked the two sculptors' careers. While Soares dos Reis remained rooted in the Portuguese art world, where he faced financial constraints and limited public commissions, Saint-Gaudens found greater institutional and governmental support in the United States. He gained considerable recognition and was often commissioned to produce public monuments celebrating historical and political figures.

Materially, their practices also diverged. Soares dos Reis was a master of marble carving and personally executed many of his works in stone. In contrast, Saint-Gaudens transitioned to bronze as his preferred medium from the late 1870s onwards, beginning with the *Farragut Monument* in New York (Greenthal, 1985). This shift reflected broader trends in American public sculpture at the time, which increasingly favoured durable, cast materials for urban and commemorative spaces.

Their legacies, while both rooted in rigorous academic training, reflect distinct trajectories shaped by national context and available opportunities. Whereas Soares dos Reis left a lasting imprint on Portuguese academic sculpture and education, Saint-Gaudens became a central figure in the American commemorative tradition, blending classical form with national narrative in ways that helped define the visual identity of the United States in the post-Civil War period.

2.5.3 Auguste Rodin

Auguste Rodin (1840–1917) represents a fundamental shift from both Soares dos Reis and his contemporaries. Widely regarded as one of the most influential sculptors in modern history, Rodin challenged the conventions of academic sculpture through a deeply expressive and experimental approach that set him apart from the academic orthodoxy of the 19th century.

Unlike Soares dos Reis, who received formal training at the APBA and the École des Beaux-Arts, Rodin was rejected three times by the latter institution. His artistic education was shaped instead at the *Petite École*[19] and through years of professional experience as an

[19] The *Petite École*, officially known as the *École de Dessin et de Mathématiques de Paris*, was an educational institution established in 1766. Between 1832 and 1866, this school offered courses in decorative sculpture, playing a crucial role in the training of future sculptors. Many students who completed this course continued

assistant in workshops and decorative arts studios (Abdel Nabi et al., 2021; Janson, 1985). This unconventional training freed him from the rigid academic ideal of the human figure, allowing him to pursue a sculptural language focused on emotional expression, naturalistic modelling, and physical dynamism.

As Rainer Maria Rilke (1948) noted, Rodin understood that the central aspect of his work was the human body, making the forms and expressions of its surface his primary focus of study. Unlike academic sculptors trained at institutions such as the École des Beaux-Arts, Rodin developed outside that system, which allowed him to avoid the rigid norms imposed by academic teaching. Lawton (1906) described the academic nude as a fixed structure of exact measurements and proportions, where any deviation was considered incorrect or unacceptable. Free from these constraints, Rodin preserved the originality of his forms, creating more expressive, dynamic, and often exaggerated figures. This contrast with Soares dos Reis, who remained within the bounds of academic realism, reveals a fundamental difference in their sculptural approaches.

Rodin's studio practice was remarkably prolific and thoroughly documented. Numerous sources, such as photographs, drawings, interviews, and written correspondence, offer insight into his working methods and artistic philosophy (Getsy, 2021). Conversations with the critic Paul Gsell and the poet Rainer Maria Rilke, who also served as his secretary, have further enriched the understanding of his creative process.

These materials reveal that Rodin maintained a dynamic and collaborative workshop, with a scale and organisation that set him apart from many of his contemporaries. While Soares dos Reis, despite his artistic talent, faced financial limitations that restricted his access to models and assistants, Rodin's growing recognition and commissions allowed him to employ a substantial team of collaborators. Before 1880, his workshop included just four assistants; by 1900, this number had grown to nearly fifty (Rosenfeld, 1981). The team comprised

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their education in sculpture, considering the Petite École as a preliminary step towards the École des Beaux-Arts. Among its notable alumni were renowned sculptors such as Auguste Rodin, Jean-Baptiste Carpeaux, Henri Chapu, and Jules Dalou (Paz, 2021).

expert mould-makers, finishers, skilled assistants, and apprentice sculptors, who executed many of the technical phases of his work.

In addition to his technical staff, Rodin maintained a large number of live models, whom he observed and sketched extensively as part of his creative process (Abdel Nabi et al., 2021; Elsen, 1972). These observations directly informed his work in clay, wax, and plaster, allowing him to capture expressive gestures and anatomical subtleties of the human form. They also served as the basis for subsequent sculptural developments. In this process, his assistants were responsible for preparing adjustable armatures, which enabled the repositioning of forms and facilitated sculptural experimentation (Sanders, 1977).

Once a model was finalised, Rodin commissioned mould-makers to produce plaster casts, allowing for further modifications or reproductions (Sanders, 1977). These plaster pieces were rarely treated as unique works, they could be repositioned, cut, recombined, or integrated into new compositions in a practice known as assemblage (Butler, 1993; Getsy, 2021; The Clark Museum, 2022). This flexibility gave Rodin's plaster works a greater creative potential, allowing him to explore multiple artistic possibilities from a single piece and significantly expanding his capacity for experimentation.

Rodin frequently employed marble and bronze as the final materials for his sculptures, each chosen for its particular expressive and symbolic potential. Marble, associated with classical tradition and permanence, contributed significantly to the recognition Rodin received during his career. Bronze, by contrast, allowed for greater formal experimentation, detailed surface modelling, and serial reproduction, becoming increasingly important in his later production through the use of the lost-wax casting technique.

In his marble sculptures, although there are works created during Rodin’s early years as a sculptor, the majority were executed by assistants and apprentice sculptors under his supervision. Rodin himself focused primarily on the modelling phase using clay, wax, or plaster (Abdel Nabi et al., 2021; Getsy, 2021; Lawton, 1906; Rosenfeld, 1981). In some cases, it is challenging to ascertain which marble pieces were executed by the artist and which by his workshop (Butler, 1993; Rosenfeld, 1981; Sanders, 1977). While both Rodin

and Soares dos Reis were highly skilled modellers, Soares dos Reis was also a master marble carver who executed many of his own works in stone, whereas Rodin typically delegated that task to trained specialists.

In relation to his bronze works, Rodin collaborated with a wide network of foundries, establishing formal contracts for both the full-scale casting of his sculptures and their reductions. Among the foundries he worked with were the Compagnie des Bronzes in Belgium; the Gruet Jeune Foundry, followed by Adolphe Gruet; the F. Liard Foundry; Pierre Bingen's Foundry; the Griffoul and Lorge Foundries; Eugène Gonod's Foundry; the Société Anonyme de Fonderie Artistique; Fumière et Gavignot; L. Gasne; Léon Perzinka; Leblanc-Barbedienne; and, from 1902 until the artist's death, the Alexis Rudier Foundry (Laurent, 1981).

Rodin favoured the lost-wax technique, a method that had been revived in the 19th century and was valued for its artisanal precision and capacity to preserve surface detail. This process involved creating a wax positive of the sculpture, which allowed the artist to make final refinements before casting. This flexibility offered a high degree of control over the final result, which was particularly important to Rodin given his emphasis on texture and expressive modelling (Sanders, 1977).

One of Rodin's most effective strategies was the use of plaster models to create serial reproductions of his works, particularly his statuettes (Abdel Nabi et al., 2021; Getsy, 2021). These plaster models played a crucial role in enabling the production of multiple bronze versions in varied sizes. By serving as adaptable intermediaries, they allowed for the rescaling of original pieces, facilitating reproductions that catered to the preferences of both public and private collectors. A notable example is *The Kiss*, of which more than 300 authorised bronze casts were produced during his lifetime (Victoria & Albert Museum, n.d.).

Rodin also embraced the technological innovations of his time, using photography both as a creative tool and as a commercial and documentary medium. This extensive visual documentation, comprising portraits, studio views, exhibition records, and work-in-progress images, offers crucial insight into his methods and into the public narrative he constructed

around his art. Through these images, Rodin not only recorded his creative process but also shaped how his work was received and remembered (Abdel Nabi et al., 2021; Elsen, 1981).

Rodin was not only a renowned sculptor, but also a strategic self-promoter with a clear commercial vision, who deliberately shaped and projected his public image as a creative genius. He understood the importance of narrative and visibility in building an artistic legacy, carefully curating his persona to align with ideals of modern authorship and innovation. This self-fashioning played a crucial role in the expansion of his career and in the consolidation of his international reputation. In a pioneering move for his time, Rodin organised retrospectives of his work, renting and customising exhibition pavilions to create immersive environments that allowed visitors to engage intimately with his creative process (Souter, 2021). These exhibitions functioned not only as cultural events, but also as calculated acts of branding that positioned Rodin at the forefront of modern sculpture.

As his reputation solidified, Rodin was invited to exhibit in various European cities, where he successfully sold several pieces to municipal institutions (Butler, 1993). To make his work more accessible and commercially viable, he produced scaled versions of his sculptures in different sizes and materials, especially in marble and bronze (The Clark Museum, 2022). This diversification strategy broadened his audience and allowed his art to circulate beyond elite collectors and public commissions.

This overview of the creative processes of Teixeira Lopes, Saint-Gaudens, and Rodin offers a comparative framework through which to better understand the singularity of Soares dos Reis' artistic practice. While each of these sculptors operated within distinct artistic and cultural contexts, the analysis of their methods, ranging from academic discipline to experimental innovation, sheds light on broader 19th-century sculptural currents. These parallels and divergences provide a richer perspective on the methodological landscape in which Soares dos Reis developed his work.

2.6 BRONZE SCULPTURE: MATERIALS, CASTING TECHNIQUES, AND TECHNICAL PRACTICE

Following the exploration of the creative processes of Soares dos Reis and his contemporaries, it becomes pertinent to examine the technical approaches that complete the sculptural process. Among these, bronze casting occupies a particularly significant place. This is not only due to its symbolic and historical relevance in the field of sculpture, but also because it marks the moment where artistic vision meets technical execution.

Bronze has been used since antiquity for works ranging from small, detailed figures to monumental public sculptures. Its enduring appeal lies in its versatility, strength, durability, and resistance to environmental degradation. It is also appreciated for the beauty and nobility of the material itself. Over time, bronze develops a distinctive green patina, a feature valued both for its aesthetic effect and for its protective function.

Although this section does not focus directly on the work of Soares dos Reis, the detailed analysis of modern casting methods, some of which were observed first-hand in Portuguese foundries during this research, offers a broader understanding of the technical context in which bronze sculptures, including those by the artist, were and continue to be produced.

2.6.1 Alloys in Sculpture Casting

In sculptural practice, copper alloys present a wide range of compositional variations depending on the proportions and types of elements used. The most commonly employed alloys are copper-tin (traditionally called bronze) and copper-zinc (brass), both of which may also include minor additions of elements such as lead or arsenic to enhance specific properties, including malleability, mechanical strength, and resistance to high temperatures.

Despite the technical differences between these alloys, in the field of sculpture the term *bronze* is often used generically to refer to any copper-based alloy used for casting (Pouyet et al., 2019). This usage is rooted more in historical convention than in strict metallurgical classification. Understanding the nuances of these compositions is essential not only for conservation and analysis, but also for interpreting the technical choices made by sculptors and founders throughout history.

Copper

Copper is the primary component in the alloys examined in this work. Classified as a noble metal, alongside gold and silver, it is recognised for its distinctive reddish hue, malleability, and excellent electrical and thermal conductivity. These properties, along with its corrosion resistance, have made it one of the most valued materials in both artistic and technological contexts since antiquity.

In nature, copper is found in its native metallic state or within minerals such as chalcopyrite ($CuFeS_2$), cuprite (Cu_2O), chalcocite (Cu_2S), malachite ($Cu_2CO_3(OH)_2$), azurite ($Cu_3(CO_3)_2(OH)_2$), and pyrite (FeS_2) (Cardoso, 1976; L. Selwyn, 2004). It is often associated with elements such as lead, nickel, silver, and zinc (Marušić, 2011).

Archaeological evidence suggests that copper was one of the first metals used by humans. Its earliest documented use dates to around 8700 BCE at the site of Çayönü Tepesi in Anatolia (Davis, 2001; Kassianidou & Knapp, 2005; L. Selwyn, 2004). Initially worked through cold hammering, cast copper objects began to appear around 7000 BCE, also in Anatolia (Davis, 2001).

In Portugal, one of the main copper mining areas was in Alentejo, particularly the São Domingos mine in Mértola. This pyritic deposit, among the most significant in the region, extends approximately 60 km and spans both Portuguese and Spanish territory. It was exploited for copper, zinc, lead, and sulphur from the first millennium BCE until its closure in 1966 (Guita, 2011). Additionally, objects made from copper and tin alloys have been

discovered at the Cachouça site in Castelo Branco, central Portugal, indicating the presence of a local metallurgical centre at the end of the Bronze Age and the beginning of the Iron Age (Bottaini & Vilaça, 2022).

Among the key physical properties of copper, its exceptional electrical and thermal conductivity stands out, being the highest among common metals. Copper is a hard, tough, and highly malleable material, capable of being worked into extremely thin sheets through hammering (Cardoso, 1976). Its melting point is 1084 °C, and its boiling point reaches 2310 °C (Cardoso, 1976; Clerin, 2000). The mechanical strength of copper and its alloys depends on temperature: a moderate reduction in strength is observed when the metal is heated to around 200 °C, with a more significant decrease occurring near 400 °C (M. Li & Zinkle, 2012).

Copper's ability to resist corrosion is among its most valued properties and has ensured its widespread use since antiquity. In dry environments, copper remains largely stable when exposed to oxygen. In humid conditions, it first develops a reddish-brown layer of cuprite, which over time can evolve into a greenish patina. This patina, highly regarded for its aesthetic effect, also serves as a protective barrier in low-pollution settings, though it may become corrosive in more polluted atmospheres.

This durability made copper a material of choice for practical applications in the ancient world. For instance, the Egyptians employed copper bands and nails in shipbuilding and piping systems, demonstrating an early understanding of the metal’s resilience and unique properties (Massey et al., 1973).

Copper – Tin alloy

Commonly known as bronze, this is one of the oldest and most widely used alloys in sculpture. It consists primarily of copper and tin, although some commercial variants include small quantities of other elements, such as zinc and lead (Fredj et al., 2013; Ghali et al., 2007).

Depending on the tin content, the colour of the alloy can vary, ranging from a reddish-yellow tone in bronzes with low tin concentrations to a paler, whitish hue in those with higher tin percentages (Cardoso, 1976; Rich, 1988). A classic bronze composition, with 88% copper, 10% tin, and 2% zinc, exhibits a distinctive reddish tone (Rich, 1988).

The inclusion of tin significantly improves the properties of the alloy. It increases hardness and resistance to corrosion, enhances the flowability of the molten metal, and provides excellent wear resistance. Tin also contributes to lowering the alloy's melting point, which typically ranges between 950 °C and 1000 °C (Clerin, 2000; Giumlia-Mair, 2012; Non-Ferrous Founders' Society & Copper Development Association, 1994; Rich, 1988; Romero & García Solé, 2008). Other elements may be added in smaller proportions to further tailor the alloy's characteristics (Rich, 1988).

The development of bronze metallurgy represents one of the earliest technological innovations in human history. Objects made from copper-tin alloys have been discovered in Thailand (c. 4500 BCE) and the Middle East (c. 3000 BCE). In China and Japan, similar objects appear around 1600 BCE, indicating that bronze metallurgy may have originated in the Far East before spreading westward (Clerin, 2000; Davis, 2001).

From these Eastern regions, bronze metallurgy was progressively adopted in other parts of the world, accompanied by significant advancements that facilitated its production. For instance, the addition of lead lowered the alloy's melting point and improved its flowability and machinability (Kuyucak & Sahoo, 1996).

Historically, the copper-tin alloy became the preferred material for sculpture, particularly in Ancient Greece. Sculptors such as Polykleitos, Lysippos, and Myron worked primarily in bronze, using casting techniques and, in some cases, hammering bronze sheets over wooden cores (Clerin, 2000; Rich, 1988).

The use of copper-tin bronze continued into the 19th century (As artes do metal, 1910; Barinaga, 1874; Magne, 1917). A notable example is the bust of *Francisco de Almada e*

Mendonça by António Soares dos Reis, cast in bronze with a high tin content. This work will be analysed in detail in Chapter 5.

Copper–Zinc Alloy

Also known as brass, the copper–zinc alloy is recognised for its distinctive yellowish colour, which varies depending on the zinc content in its composition. This proportion can range from 5% to 45%, influencing both the appearance and physical properties of the alloy. Brass with less than 10% zinc tends to appear reddish, between 10% and 15% it takes on a golden tone, and above 20% it shifts to a silvery white, approaching grey as it nears 40% zinc (Clerin, 2000; Davis, 2001; Rich, 1988).

The use of brass in European artistic contexts dates back to the 13th century, initially applied in memorial bas-reliefs. These were typically created by embossing brass sheets, which were then affixed to stone surfaces (Rich, 1988).

Over time, brass gained popularity, and by the 19th century, it had become one of the preferred alloys for sculpture, largely due to its excellent fluidity when molten, a property similar to tin but more economical (Davis, 2001; Pouyet et al., 2019). Brass also offers strong corrosion resistance, a key characteristic for sculptures displayed outdoors.

For sculptural purposes, the optimal zinc content lies between 7% and 15%, as this range retains the alloy's malleability and ductility. Beyond these values, the material becomes increasingly brittle, reducing its workability (Davis, 2001; Rich, 1988).

A particularly valued variant in sculpture is Fine Casting Brass, which contains approximately 90% copper, 7% zinc, 2% tin, and 1% lead (Rich, 1988). This composition balances mechanical strength and aesthetic appeal, making it ideal for producing detailed and durable works.

It is important to note that in Portugal, the composition of copper alloys used in sculpture varies depending on their source. Some companies purchase certified bronze, such as *silicon bronze*, while others use metals sourced from scrapyards to produce alloys, thereby reducing production costs. Consequently, the validation process for the alloy used in creating a piece largely depends on the foundry worker's expertise. For this reason, the only reliable way to accurately determine the composition of a sculpture is through analytical methods, such as X-ray fluorescence, which has been employed in this study (C. Bernardino, personal communication, February 2021; R. Palmas, personal communication, 10 November 2020; Portela de Castro & Junqueira, 1996).

During casting, the melting temperature of copper–zinc–tin alloys depend on their specific composition. For modern sculptures, the minimum melting point is about 900°C, with an average around 970°C (Villar González, 2010). In alloys with low zinc content, the temperature may reach approximately 1100°C (Pouyet et al., 2019).

To further improve the physical and mechanical properties of the alloy, small quantities of other elements are often added. For instance, lead increases machinability by forming small lubricating droplets (Boldyrev, 2018), while arsenic enhances resistance to corrosion and high temperatures (H. Zhang et al., 2021).

However, some of these elements pose health and environmental risks during the casting process. For this reason, safer alternatives such as bismuth are now used in place of lead to improve mechanical performance (Han et al., 2012).

2.6.2 Bronze Casting Methods in Sculpture

The development of metallurgical techniques in antiquity, particularly the discovery of lost-wax casting, marked a major advancement in the use of bronze for artistic, domestic, and military purposes.

It is estimated that this technique emerged simultaneously in various regions, including Anatolia, the Iranian plateau, Syria, and Palestine, in the late third millennium BCE, signalling the beginning of the Bronze Age (Clerin, 2000; Hunt, 1980). In Mesopotamia and other parts of the Near East and the Aegean, lost-wax casting underwent significant refinement during this same period (Hunt, 1980). In these regions, the smelting of copper and its alloying with arsenic, and later 8% tin, had already become part of an established large-scale industry by 3000 BCE (Kassianidou & Knapp, 2005).

Lost-wax casting was also adopted by the Phoenicians, active across North Africa and along the Mediterranean coasts of Italy, Sardinia, Sicily, and the Balearic Islands from around 900 BCE. The Etruscans, with close trade ties to the Greeks and Phoenicians, incorporated this technique around 800 BCE. In the north, the Celts developed and expanded its use, influenced by the Scythians (Hunt, 1980).

In the Iberian Peninsula, evidence of bronze casting using alloys (copper, tin and lead) has been found in Galicia, dated between 900 and 550 BCE, corresponding to the final stages of the Bronze Age (Sierra Rodriguez, 1978). In the region of Trás-os-Montes in northern Portugal, archaeological excavations have revealed evidence of metallurgical activity. At the site of Sola (Braga), remains of furnaces, fire pits, and a copper alloy rod were found, dating to the 17th–16th centuries BCE (Vieira, 2014).

Early casting moulds also underwent a gradual evolution. Initially, molten copper was poured into rudimentary stone or clay moulds (Hunt, 1980).



Fig. 2.5 - Stone mould used for casting weapons and tools. Nuragic culture, Late Bronze Age. Museo Archeologico Nazionale di Cagliari, Sardinia, Italy. © *Pablo General-Toro.*

In contemporary practice, however, although numerous casting methods exist due to technological advances, lost-wax casting and sand casting remain the most widely used in sculpture. The choice between these techniques depends on the dimensions, level of detail, and specific characteristics of the piece.

All casting techniques, regardless of their specific characteristics, share a common principle. The metal is heated in a crucible until it reaches its melting point, then carefully poured into a prepared mould where it is left to cool and solidify. Once solid, the piece is extracted and subjected to cold working processes to refine its surface and achieve the final artistic result (Clerin, 2000; Midgley, 1993).

Sculptures produced by casting are typically hollow, whether using lost-wax or sand casting. This approach offers economic, practical, and structural advantages. Hollow pieces require less metal, are significantly lighter, and are less likely to crack during cooling, especially in areas with irregular geometry (Mills, 1990).

Variations in wall thickness within hollow casts can lead to uneven cooling, increasing the risk of fractures. To address this, internal armatures made of the same alloy are inserted to act as chill bars, helping thicker areas cool at the same rate as thinner sections (Mills, 1990).

As part of this research, modern foundry techniques were examined through site visits to Bernardino Fundição D'Arte, Fundição do Regato, CINFU (Centro de Formação Profissional da Indústria de Fundição), and Fundição Mão de Fogo. These institutions generously offered access to their facilities between 2020 and 2024, enabling the observation of contemporary artistic and industrial casting practices.

2.6.3 Lost wax casting

Lost-wax casting is widely used for producing sculptures with intricate forms (Peláez, 2003). Sculptures made using this method can be either solid or hollow, depending largely on their size. Solid casts are subject to limitations due to issues like shrinkage, internal stresses from uneven cooling, and potential distortion as the metal sets. These stresses can lead to cracking or deformation. For solid bronze sculptures, it is generally recommended that the thickness does not exceed 2.5 centimetres, and the height is limited to between 25 and 30 centimetres (Midgley, 1993).

Creation of the wax model

Once the plaster model has been completed by the mould-maker, the next step is to create a negative mould. Traditionally, this was made from ceramic plaster. Today, however, silicone is the preferred material because it can be reused many times without wearing out, and it provides an accurate reproduction of the original form.

Silicone's flexibility and stretchability make it suitable for both simple and complex shapes. It also removes the need to divide the mould into smaller parts. In contrast, traditional plaster moulds often required inserts to help with demoulding, especially for more detailed forms.

The mould generally consists of two sections, front and back (Fig. 2.6), joined through keyed seams that ensure precise alignment, guaranteeing a faithful duplication of the original model (Fig. 2.6a).

Silicone moulds, due to their flexibility and elasticity, and plaster moulds, which are often composed of multiple pieces, require a plaster structure that acts as a supporting shell. This shell maintains the mould in place during the subsequent procedures. The structure, composed of two halves (Fig. 2.6b), includes a fastening system that secures the shell to the

mould (Fig. 2.6c), ensuring a firm connection between the shell's halves (Fig. 2.6d). This prevents any displacement that could compromise the mould's position.

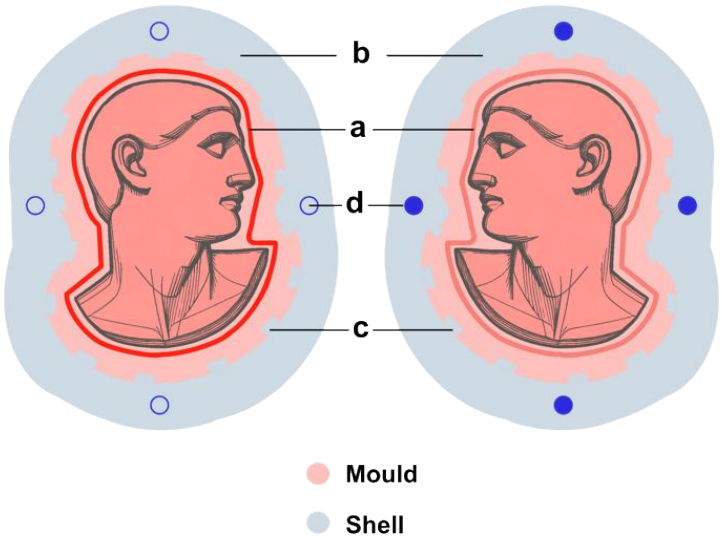


Fig. 2.6 a-d - A two-part silicone mould: front and back. Area A shows the joint section between the two parts of the mould; area B corresponds to the supporting shell, area C indicates the attachment points between the mould and the shell, and point D highlights the fastening systems between the two halves of the shell.

For both plaster and silicone moulds, it is necessary to apply a thin layer of a greasy release agent to the original model beforehand, facilitating demoulding without damaging the wax model.

In the case of more complex pieces, particularly those with irregular surfaces featuring reliefs and recesses, silicone moulds are typically cut in strategic areas to facilitate the demoulding process.

Once the mould is completed, the creation of the wax walls of the figure begins. This process starts with the application of successive layers of wax onto the mould's surface using a brush (Fig. 2.7). The wax typically used is microcrystalline wax, primarily due to its affordability. This type of wax is available in various pigmentations, tailored to its physical, mechanical,

and chemical properties (Carrero, 2013). In some foundries visited in Portugal, the wax mixture includes beeswax, paraffin, and other additives intended to improve its performance.



Fig. 2.7



Fig. 2.8

Fig. 2.7 - Appearance of the silicone mould after several layers of liquid wax have been applied with a brush. © *Pablo General-Toro.*

Fig. 2.8 - Joining of the two parts of the silicone mould, fitted into the plaster shell and secured with straps to prevent separation or displacement. © *Pablo General-Toro.*

The two halves of the mould are then brought together. A greasy material is applied to the areas where the plaster shell meets to make it easier to separate later on. The outer shell is securely fastened to prevent the mould from opening unintentionally (Fig. 2.8).

With the mould closed, liquid wax is poured inside to seal the joints and gradually build up the wall thickness (Fig. 2.9a). The wax is gently moved around to ensure it coats the entire surface evenly, and any excess is removed. This process creates a uniform wax layer inside the mould (Fig. 2.9b). It is repeated several times until a wall thickness of approximately 3 to 4 millimetres is achieved. This thickness is typical of hollow sculptures, which require a consistent and controlled layer to provide both structural stability and the proper conditions for casting.



a b

Fig. 2.9 - Pouring liquid wax into the closed negative mould to increase the wall thickness (a), followed by the removal of excess wax from the interior of the figure (b). © *Pablo General-Toro.*

Once the wax has cooled and hardened, the model is removed from the mould. It is then carefully checked to remove any burrs and to correct small surface flaws.

After that, the inside of the wax model is filled with a type of refractory plaster. This will form the inner core, or *macho*, that defines the space to be cast.

If the model doesn't already have an opening for introducing the core material, small square holes are made in areas that are less visible (Fig. 2.10 – 2.11, grey). These temporary core access holes allow the refractory plaster to be poured in to form the inner core. After casting, they also serve as points of access for removing the hardened core material.

The wax fragments removed when opening these holes, referred to as core access plugs, are attached to the sprue system and cast in bronze as well (Fig. Fig. 2.10 – 2.11, blue). Once the sculpture is complete, these pieces, now in bronze, are welded back into place to restore the continuity of the surface.

In the past, to support the inner core of a hollow wax model, a kind of internal framework or skeleton was used. The cavity was filled with a mix of earth, debris, brick dust and horse

manure, which helped to support the core and fill any gaps. This inner mass, roughly shaped like the final model, was then hardened by baking (Peláez, 2003). Today, the core is made of refractory material similar to that used for the mould. It is held in place by metal rods, which support it during the firing process when the wax is burned out (Clerin, 2000).

Preparation of the sprue tree

The next stage involves building the sprue tree, with the wax model placed at its centre. This system is designed to guide the molten copper alloy through every detail of the sculpture (Fig. 2.10). The correct design of the sprue tree is essential, as it ensures that the metal enters and flows evenly throughout the mould.

The sprue tree (Fig. 2.11) is made up of a funnel (red), which is the entry point for the molten metal, a main sprue (brown) that carries the metal downward, and a network of feeders (light green) and runners (dark green) that distribute the metal throughout the mould. Vents (light blue) are also included to allow air and steam to escape, preventing the formation of bubbles or unfilled areas.

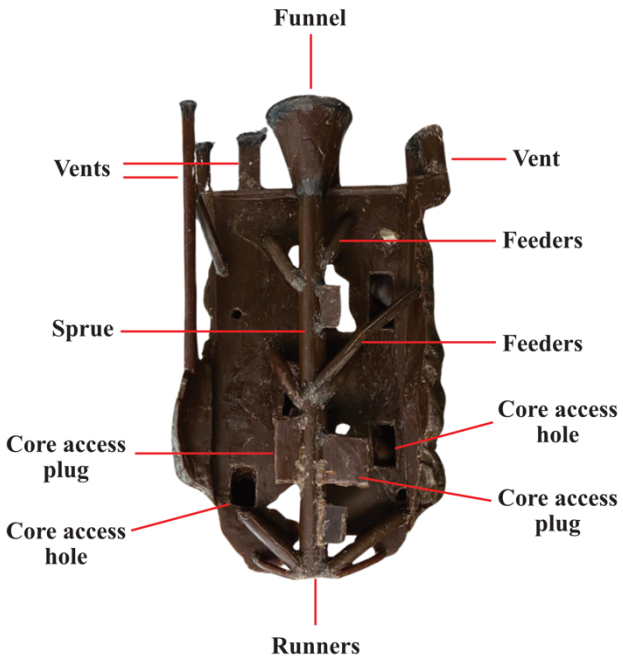


Fig. 2.10 - Reverse side of a wax sculpture, where the components of the sprue tree are visible. During the removal of the wax, the sculpture is kept in this position. For the bronze casting, the mould is inverted, placing the funnel upwards to pour the molten metal.

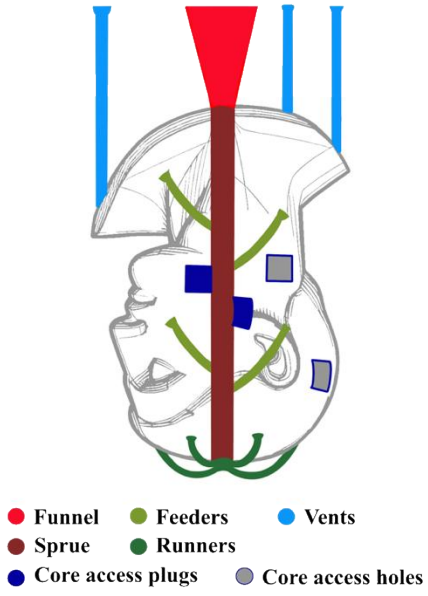


Fig. 2.11 - Diagram of the areas that make up the simple sprue tree in a sculpture.

For these channels, flexible wax rods of various thicknesses are used. Their size and positioning are adjusted based on the sculpture's dimensions and the function of each element (Fig. 2.12). The rods used for feeders and vents must be tailored not only in diameter but also in length, which increases in proportion to the width to ensure smooth metal flow (Clerin, 2000).



Fig. 2.12 - Wax rods and cones used to form the sprue tree.
© Pablo General-Toro.

The feeders, also known as pouring channels, are made from thicker wax rods and are placed strategically on the wax model, depending on the structural features of the piece. These converge at the central sprue, which acts as the main path for the molten metal. Towards the upper parts of the sculpture and at the extremities, thinner rods are attached to act as vents. These allow trapped air and gases generated during casting to escape. It is important that the vents are always positioned upwards, as this orientation helps to release gases efficiently and prevents voids or bubbles from forming in the final bronze cast (Carrero, 2013; Manso, 2011; Midgley, 1993).

Creation of the Casting Mould

Metal nails are driven into the wax figure, already containing the core inside, serving as anchors that connect the wax, the core, and the mould once it is applied. These anchors will help keep in place the space left by the wax when it is removed from the mould.

The quality of the casting of a piece made using the lost wax technique is crucial and is intrinsically linked to both the fidelity of the wax model and the quality of the refractory material used for the mould. Any irregularity present in the mould will be directly reflected in the final sculpture, potentially leading to damage to the work (Manso, 2011). The precision and quality of the materials used in this process, play a key role in ensuring the success and integrity of the sculpture's reproduction.

There are two main types of moulds used in the lost wax casting process: the poured mould and the shell mould.

The poured mould (Fig. 2.13) is primarily used for smaller sculptures and jewellery pieces. This technique involves pouring refractory plaster over the wax figure and the feeding system. The figure is placed inside a container or mould designed to create the appropriate thickness of the plaster mould.

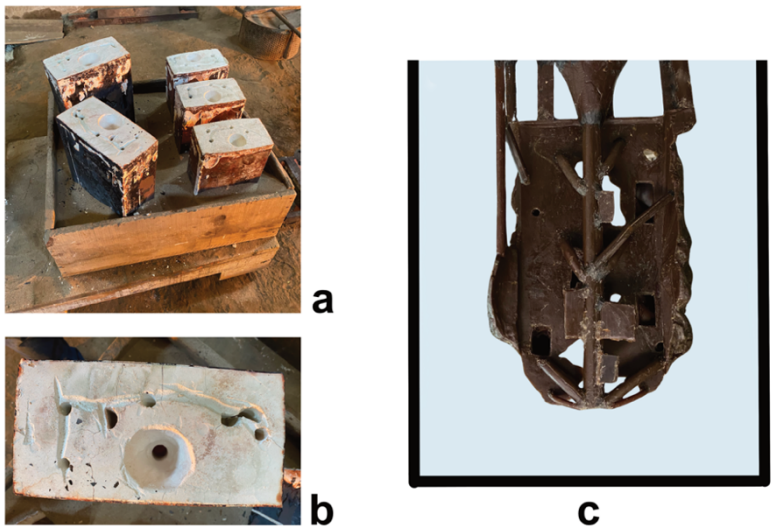


Fig. 2.13 a,b,c - (a) Moulds prepared for bronze casting; (b) detail of the funnel for bronze inlet, and air/gas vents; (c) diagram showing the wax model inside the mould. © *Pablo General-Toro.*

Subsequently, ceramic plaster or refractory plaster is carefully poured, avoiding direct contact with the wax model. The plaster must cover the entire model, reaching the ventilation rods. It is important to leave the access points of these rods and the funnel visible to facilitate the subsequent bronze casting process (Carrero, 2013).

It is desirable for the creation of this mould to be carried out under certain vacuum conditions to prevent the formation of bubbles in the mould. Bubbles formed on the surface of the wax figure can affect the final bronze model, both in its shape and in the time required to remove the shapes of these bubbles, cast in bronze, during the metalwork stage (C. Bernardino, personal communication, 30 March 2021).

To improve the adhesion of the refractory material to the wax, a solution of soap diluted in water can be applied. Additionally, some foundry workers reinforce the union between the initial and secondary layers of this type of mould using wire mesh (Carrero, 2013; Clerin, 2000).

The ceramic shell mould uses a progressive coating process that gradually reinforces the structure. In this method, the wax figure and its feeding system are completely covered with layers ceramic slurry applied with brush (Fig. 2.14). The aim of this process is to produce a mould as faithful as possible to the original model, which helps achieve a homogeneous surface and prevents the formation of bubbles (Clerin, 2000; Manso, 2011).



Fig. 2.14 - First layer of ceramic plaster applied with brush to a piece to accurately reproduce all the details of the original surface. *© Jeremy Thompson. Image provided by Carolina Bronze (carolinabronze.com).*

Subsequently, the figure is submerged in a slurry of refractory ceramic slurry (Fig. 2.15a), and then sprinkled with silica sand to create an initial durable layer (Fig. 2.15b). This process is repeated in several layers, allowing each one to dry before adding the next (C. Bernardino, personal communication, 30 March 2021). In this way, a shell or casing is formed that, once hardened, is strong enough to withstand the weight and heat of the molten bronze during the final pour (Fig. 2.16).



Fig. 2.15 a, b - a) Immersion of the mould in a container of ceramic slurry. b) Application of the first layer of silica sand to the surface. *© Jeremy Thompson. Image provided by Carolina Bronze (carolinabronze.com).*



Fig. 2.16 a-d - Application of ceramic slurry and silica sand to the mould and casting tree, showing the gradual formation of the ceramic shell. © *Jeremy Thompson, courtesy of Carolina Bronze (carolinabronze.com).*

Once the mould has dried and solidified, the cleaning of its surface is carried out, with particular attention given to the holes of the feeding channels and vents. The surface of the mould must be smoothed and rounded to remove any protruding areas that could compromise its strength and cause fragility (Manso, 2011).

Before starting the firing process, it is crucial to keep the interior of the mould moist. This moisture acts as an effective barrier against the penetration of wax into the refractory material during its melting. It is recommended to carry out the firing immediately after the mould has dried. If this is not feasible, it is advisable to spray the mould with water and cover it with plastic to preserve its moisture (Clerin, 2000; Manso, 2011).

The choice of one casting technique over another depends on the country and the materials available. In Portugal, the shell mould or *carapaça* is used in the production of high-quality tools that require exceptional precision, being especially employed in the creation of components for the aviation industry and the healthcare sector.

The lost wax casting process using a shell mould is optimal for the mass production of pieces. However, this process has a significant disadvantage: the drying of the ceramic structure can take up to a week. This is because each layer of material applied to the wax model must be completely dried before the next can be applied. Furthermore, this method requires the continuous operation of the equipment that maintains the silica-based ceramic slurry in a usable state (C. Bernardino, personal communication, 30 March 2021).

In the creation of sculptures, Bernardino Fundição d'Arte, one of the foundries visited, employs the block pouring process. Unlike the shell mould technique, in this method, the plaster is applied all at once. After drying, the mould undergoes firing, allowing the cast piece to be ready within 24 hours. This time optimisation contributes to improved economic benefits for the company (C. Bernardino, personal communication, 30 March 2021).

Firing of the mould

The removal of the wax in the lost-wax casting process is carried out through its melting. This procedure results in the disappearance of the wax model, leaving a cavity in the mould. This space will be filled by the molten metal, which is introduced through feeding channels or sprues.

The furnace used for the firing and drying of the mould, known as a *muffle furnace*, gradually increases its temperature, allowing for precise control of the thermal rise. This control is crucial to prevent the mould from breaking and facilitates the evacuation of the wax through a hole in the lower part of the furnace. Additionally, the process ensures the complete removal of the water contained in the mould, a vital step to prevent the formation of porosities or defects in the finished piece.

During the mould firing process, the furnace can reach a temperature ranging from 650 to 800 °C. The duration of the firing depends on the size of the mould and the power of the furnace. For small sculptures, with a quick firing process, the procedure may take around ten hours, while for larger moulds, where the firing temperature is gradual, the process can last up to four days (Carrero, 2013; Villar González, 2010).

Metal pouring and removal of the bronze sculpture

When the moulds are ready, they are placed in a pit or sand box. This support serves to absorb the impact of the molten metal, ensuring stability and preventing fractures in the mould during the pouring process. Simultaneously, the metal alloy is melted in a graphite and silicon carbide crucible, a highly refractory material capable of withstanding extreme temperatures.

Once the appropriate temperature is reached, the crucible is removed from the furnace with the help of a crane. Using special tongs designed for handling, it is carefully transported to

the moulds. The liquid metal is poured slowly into the mould, a step requiring extreme precision, as any abrupt movement could compromise the structural integrity of the mould. Guided by the force of gravity, the metal flows and fills every detail of the mould cavity (Fig. 2.17).



Fig. 2.17 - Lost-wax casting on a mould created by pouring. Bernardino Fundição D'Arte. © *Pablo General-Toro.*

Once the metal has solidified, the sculpture is extracted by destroying the mould that encases it. During this process, the metalworker is responsible for removing both defects, fixing nails and the sprue tree. Additionally, the core, which was used to shape the internal cavities of the piece, is removed (Fig. 2.18).



Fig. 2.18 a-c - Metalworking workshop at Bernardino Fundição D'Arte: **a)** workspace dedicated to sculpture finishing; **b)** and **c)** details of the finishing process using hand tools. © *Pablo General-Toro.*

If windows were made in the wax model to facilitate the filling of the core, these openings are later reintegrated into the sculpture through welding. This procedure ensures the structural and visual continuity of the work, resulting in a uniform surface that, after being corrected and smoothed, is ready for the final finishing and patination stages.

2.6.4 Sand casting

Sand casting is a traditional process that, compared to lost-wax casting, is noted for its simplicity and ease of use. Historically, this method has played a crucial role, especially in the 19th century, when, as mentioned in Chapter 1, it facilitated the democratization of access to bronze works. This made it possible for Europe's middle classes to acquire pieces that had previously been reserved for the elites.

Although sand casting can capture the intricate details of a model, it does not achieve the same level of precision as lost-wax casting. However, its main advantage lies in its ability to

produce large-scale pieces, which often requires the sculpture to be divided into sections or modules, thereby facilitating the creation of monumental works.

Silica sands used in this type of casting are characterised by specific properties that simplify the process and ensure a high-quality result. These properties include:

Plasticity: Enables the sand to replicate the model's shape with precision when compacted, a feature influenced by the grain size.

Consistency: Ensures the sand retains its moulded shape, providing stability throughout the casting process.

Permeability: Allow gases generated during the pouring process, as well as trapped air within the mould box, to escape, preventing defects in the finished piece.

Refractoriness: Refers to the sand's capacity to withstand high temperatures without losing its integrity, thereby avoiding fusion or vitrification that could cause the mould to adhere to the metal.

Collapsibility: Facilitates the breakdown of the sand after the metal has solidified, allowing the mould to be removed without damaging the cast piece (García Chacón, 2016).

Before the introduction of artificial sands, the most commonly used type in casting is known as *green sand.* This material consisted primarily of natural silica sand, which was moistened for handling, then moulded and subsequently dried over a fire.

In the region of Vila Nova de Gaia, sand from the Miramar area was commonly used. This sand, rich in silica, resulted from wind-driven movements of grains, transporting the sand from the beach to inland areas where pine forests grew. Miramar sand was particularly valued for its fine grain, which allowed for the precise reproduction of surface details from the model (C. Bernardino, personal communication, 8 January 2021).

In areas near Lisbon, the sand used came from the Almada region. Although this sand did not match the quality of Miramar sand, it was widely employed, particularly in the production of bronze components used as decorative elements for furniture.

Green sand is formulated using 80 to 90% silica powder, which provides refractoriness, 4 to 9% bentonite, acting as a binder, and carbon powder. This mixture is moistened with approximately 9% water (García Chacón, 2016; R. Pinto, 2020).

Today, the most used sands are self-drying artificial sands. These are composed of silica and a binder, which react upon contact with a gas, hardening the mixture.

Mould preparation

In the sand-casting process, the sculpture model is used to create a mould that captures the form of the artwork in the sand. In some cases, particularly for more complex sculptures, the moulds may include additional detachable sections, which facilitate the demoulding process (Fig. 2.19). The mould is made using sand with a high capacity for detail reproduction, as described in previous paragraphs.

In some cases, it is necessary to manually adjust the thickness of the areas that will receive the molten bronze. This task is carried out using spatulas and relies primarily on the founder's experience, who assesses where to reinforce or reduce certain sections to ensure a uniform and technically sound casting.



Fig. 2.19 - Creation of a mould using self-drying artificial sand, with "sections" incorporated to address the complexity of the sculpture's facial features. Fundição do Regato. © *Pablo General-Toro.*

The sand mould is constructed in two halves, formed by two moulding boxes (Fig. 2.20). Traditionally, these boxes were made of iron, a robust material capable of containing green sand moulding mixtures and withstanding the high temperatures needed to dry the sand using open fires. However, over time, iron boxes have been largely replaced by wooden boxes due to their significant advantages. Unlike iron boxes, which are heavy and cumbersome to handle, wooden boxes are lighter, easier to manipulate, and more practical for modern casting processes.

Wooden boxes have gained popularity with the introduction of self-drying sands, which do not require heat to cure. These boxes are more practical than their iron counterparts, as they are lighter and easier to handle. Additionally, the use of self-drying sands has enabled greater flexibility in the size of wooden moulding boxes, allowing them to be adapted more economically and efficiently to the specific dimensions of each piece to be cast. This shift not only optimises the casting process but also reduces costs and improves production flexibility.

The two halves of the moulding box are known as the *cope* (the upper half) and the *drag* (the lower half) (Fig. 2.20 a and b).

To create the mould, sand is compacted around the model. To optimise both detail precision and material economy, fine-grain sand is used in the areas directly in contact with the model's surface, allowing for more accurate detail reproduction (Fig. 2.20c). Meanwhile, coarser-grain sand is used for the filling and support layers, which can include recycled sand from previous castings (Fig. 2.20d).

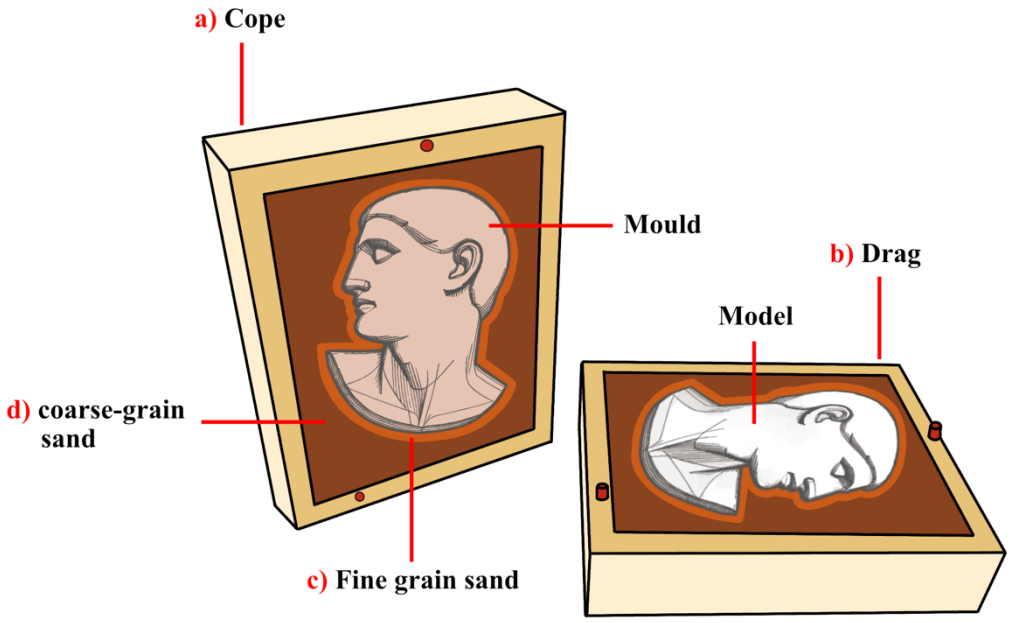


Fig. 2.20 a–d - The moulding box comprises two halves: the cope (upper) and the drag (lower) (a, b). Fine-grain sand is compacted around the model for precision (c), while coarser or recycled sand is used in structural layers (d).

Once the sand has been compacted around the model, it is carefully removed, leaving a cavity that serves as the negative or mould for the future bronze piece. At this stage, the funnel, sprue channel, feeders, vents and breathers are created, which are carved directly into the sand (Fig. 2.21). As in the lost wax casting process, these channels perform essential functions, allowing the molten metal to enter and distribute evenly while facilitating the expulsion of air and gases generated during the pouring process.

Sand casting is also used to produce complete cast pieces, although this process is mainly applied to mechanical components. In such cases, the internal core is made from the same self-hardening silica sand used for the outer mould (Fig. 2.21a). This core includes predefined connection zones with the mould, which usually correspond to internal cavities or hollow sections in the final piece (Fig. 2.21a-light blue).

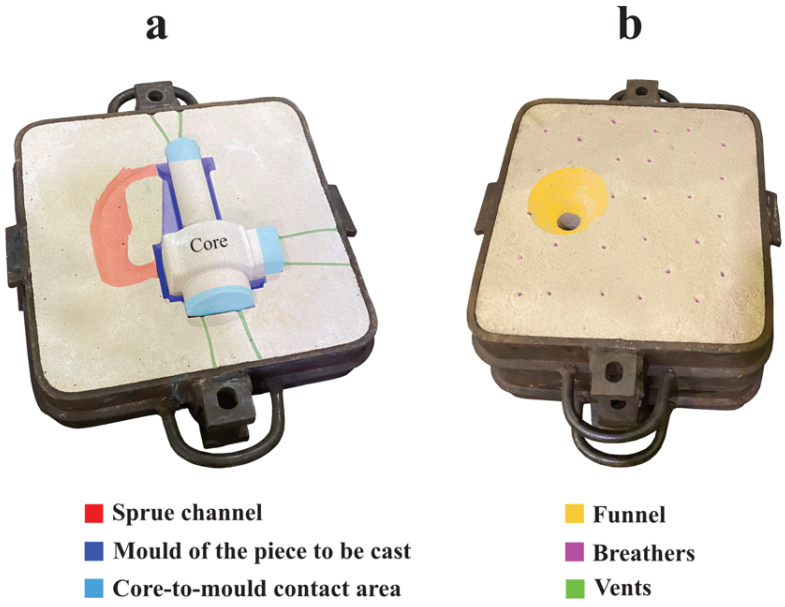


Fig. 2.2.1 a, b - Sand mould for a mechanical component. Visible features include the *sprue channel* (a-red) and *vents* (a-green), as well as the *funnel* (b-yellow) for pouring the molten metal, and the *breathers* (b-pink), which facilitate the release of air and gases.

Pouring the metal into the mould

With the mould prepared, the alloy is heated in a furnace until it reaches its melting point. Once molten, the liquid bronze contained in the crucible is transferred to the sand mould via the feeder, following the same process described in lost wax casting. The porous structure

of the sand facilitates the release of gases during the pouring process, preventing potential defects on the surface of the piece.

After the pouring process, the mould is left to cool completely, allowing the metal to solidify within the moulded cavity. Once the bronze has cooled and solidified, the sand mould is broken apart in a process known as *de-sanding*. As the sand mould is destroyed during this stage, the sculpture is revealed, exposing the bronze piece in its final form.

The resulting sculpture undergoes various finishing processes to remove imperfections and burrs that may remain on the metal surface. For sculptures made from separate pieces, artisans join these parts together using welding. However, in earlier periods, these joints were made using internal screws, followed by a surface levelling process achieved through hammering. Once the welding process is complete, the joints are carefully sanded, filed, and cleaned, ensuring the sculpture is ready for the next stage: patination.

2.6.5 Patination

Artificial patination is a deliberate and controlled corrosion process designed to form a surface layer of a specific colour on a metal artwork.

Although this corrosion effect can be achieved through the application of pigment binders to the metal surface, the most commonly used method in sculpture is the chemical method. This process significantly accelerates the corrosion of the metal alloy, enabling the formation of patina 3 to 10 times faster than would occur in an urban atmosphere (Knotkova & Kreislova, 2007; Marušić, 2011).

Artificial patination has been a common practice throughout history across various cultures, closely associated with the production of bronze sculptures and objects. Its primary aim has been to achieve specific chromatic effects through different techniques. Today, this tradition

continues, with founders using specialised chemical compounds to apply patinas to metal sculptures, adapting the processes to the characteristics of the artwork and the desired results.

The application of these reactive chemical agents induces changes in colour and texture through processes such as oxidation, reduction, temperature variations, or combinations thereof. The resulting coloration is influenced by several factors: the type of chemical used, the composition of the alloy, the thickness of the metal, the type of mould used in casting, and the artificially generated temperature during the chemical application, particularly if the patina is applied with heat (Manso, 2011; Moreno Pabón, 2008).

A wide range of chemical products is used to achieve specific tones. In Portuguese foundries, the base chemicals employed for the formation of artificial patinas include ammonia, a blue-coloured liquid based on potassium sulphide, iron nitrate, and copper nitrate (R. Palmas, personal communication, 10 November 2020). Depending on the concentration and temperature of these compounds, patinas in shades of green, blue, ochre, or red can be achieved, allowing for a wide variety of visual effects (Manso, 2011; Moreno Pabón, 2008).

Cleaning the metal surface

The application of artificial patinas to bronze pieces requires the surface to be completely clean and free of greasy residues, as these can hinder the proper adhesion of the patina or leave undesirable marks on the piece's surface.

The cleaning process begins with degreasing, for which fine abrasives bound in grease or wax can be used to smooth or polish the metal surface. Organic solvents are then applied, distributed across the surface using a nylon or wire brush. This process removes marks and impurities from holes, hard-to-reach areas, and textured or porous regions (Hughes & Rowe, 1991).

The next step involves washing the piece with water and an ammonia-free emulsion detergent. Alternatively, a more rigorous cleaning can be carried out by immersing the piece in a diluted acid or an alkaline solution (Hughes & Rowe, 1991; Manso, 2011). The process is even more complex for brass pieces, where the metal must be polished chemically or electrolytically to prevent chromatic imperfections that could compromise the quality of the final finish (Moreno Pabón, 2008).

Residues from the cleaning process must be thoroughly removed using cold running water and a fine nylon or wire-bristle brush. It is essential that the application of the chemical colouring takes place immediately after this final cleaning step. If a delay is unavoidable before beginning the patination process, it is recommended to keep the metal piece under cold running water. Any delay between cleaning and the application of the colouring can result in premature passivation and the appearance of stains on the metal surface. Should this occur, the metal piece must be properly dried, and the cleaning cycle repeated (Hughes & Rowe, 1991).

Methods of patination

There are various techniques for applying chemical compounds to create artificial patinas on metals, each designed to achieve specific chromatic effects. The compounds can be applied in different ways: by rubbing the metal surface with a cloth, using a soft brush, spraying (commonly used for large objects), or briefly immersing the piece in the chemical solution. These methods can be performed either cold or with heat, using a blowtorch (Hughes & Rowe, 1991).

The patination process using these techniques typically involves the application of several layers of the compound, with drying periods in the open air between each layer when using cold patination methods. This procedure can take anywhere from several days to weeks, depending on the number of layers applied (Hughes & Rowe, 1991).

In addition to these techniques, alternative methods can be employed, such as heat patination without the application of chemicals to achieve a dark base patina; the use of chemical vapours in a closed environment; or immersion in high-temperature solutions containing oxidising substances and copper compounds, whether acidic or alkaline (Hughes & Rowe, 1991; Knotkova & Kreislova, 2007). The choice of technique and application parameters will depend on the desired tone and finish of the metal surface.

The creation of patinas on bronze sculptures is a process that blends art and chemistry, with its success largely dependent on the collaboration between the sculptor and the founder. In many cases, the patina is applied in the sculptor's presence, allowing them to make real-time decisions about the final appearance of the work. This process is highly personalised, as the founder adjusts the application of chemical substances to achieve the tones and textures desired by the sculptor.

Although the chemical compounds used for this purpose have already been mentioned, their specific application, in terms of proportions and techniques, is often kept secret. Founders closely guard their formulas, as they represent knowledge accumulated through years of practice and experimentation. In Portugal, patinas are generally applied cold, a particular technique that adds further complexity to the process (C. Bernardino, personal communication, 8 January 2021). However, this secrecy is not the only obstacle to documenting the process; the inherent complexity of creating patinas makes it challenging to convey precisely how a particular result is achieved.

Achieving the desired finish in patina creation depends on multiple interrelated factors, such as the founder's experience and sensitivity, the specific characteristics of the sculpture, the ambient temperature, and the application conditions. These factors directly influence the chemical reactions and, consequently, the final result. Even when the same base compounds are used, their interaction with other elements and variables can produce significantly different visual effects, making each process unique (C. Bernardino, personal communication, 8 January 2021; R. Palmas, personal communication, 10 November 2020).

2.7 FINAL REMARKS ON CHAPTER 2

This chapter has provided a comprehensive overview of the artistic formation, creative methods, and technical practices of António Soares dos Reis, situating his sculptural production within a broader 19th-century artistic and material context. The analysis demonstrates that his practice, while deeply rooted in academic traditions, was marked by a personal refinement of classical methodologies that balanced technical precision with expressive form. His systematic approach, from sketching and modelling to the creation of plaster moulds, reveals a sculptor profoundly engaged with both the conceptual and material dimensions of sculpture.

By examining Soares dos Reis's techniques in dialogue with those of his contemporaries, such as Teixeira Lopes, Saint-Gaudens, and Rodin, the singularity of his sculptural vision becomes more apparent. These comparisons illustrate how shared academic foundations could lead to divergent artistic outcomes, shaped by cultural context, institutional support, and individual experimentation. Unlike the more experimental Rodin or the institutionally supported Saint-Gaudens, Soares dos Reis remained anchored in a national artistic scene that was less receptive to innovation and more constrained by economic and institutional limitations.

The chapter has also underscored the enduring relevance of classical sculptural techniques, particularly in the context of bronze casting. The detailed exploration of traditional and modern foundry practices, informed by both historical sources and contemporary fieldwork, reinforces the idea that such methods are not static relics of the past but adaptable processes still central to artistic production today.

Ultimately, this chapter establishes the necessary technical and contextual foundation for the subsequent analysis of the bronze sculptures attributed to Soares dos Reis. It highlights the interplay between artistic intent and technical execution and prepares the ground for a critical examination of the material, methodological, and conservation-related aspects of his bronze

works in the chapters that follow. In doing so, it contributes to a nuanced understanding of the relationship between artistic agency, material practices, and the technical legacy embodied in bronze sculpture.

CHAPTER 3. BRONZE SCULPTURES BY SOARES DOS REIS: SELECTED WORKS, REPRODUCTION, AND LEGAL CONTEXT

3.1 INTRODUCTION

This chapter examines the bronze sculpture of António Soares dos Reis within the context of its production, reproduction, and institutional regulation from the late 19th to the mid-20h century. Based on a specific selection of works, it establishes the corpus on which subsequent analyses will build, including observations on their casting, technique, location, and current condition.

Beyond its focus on material aspects, this chapter also examines the role played by Soares dos Reis's bronze sculptures in official reproduction initiatives led by public institutions. These practices not only contributed to extending the sculptor's presence in Portuguese public space, but also aligned with wider strategies of heritage construction and artistic recognition.

Finally, it considers the legal framework governing the reproduction of sculpture in Portugal, with particular attention to how such provisions have shaped the circulation, intervention, and posthumous legitimisation of these works. Taken together, the chapter offers a historical perspective on the factors that have determined which of Soares dos Reis's bronze sculptures

have been preserved, disseminated, or transformed, and under what political and legal conditions this has taken place.

3.2 SELECTION OF THE SCULPTURES

This research examines thirteen sculptures cast in copper alloy, each a reproduction of an original work by the sculptor Soares dos Reis. These officially sourced casts are situated in various locations in northern Portugal, specifically in the cities of Porto and Guimarães.

Table 3.1 Selected sculptures for this study, with details on their date, typology, size, and display location.

Nº	Sculpture	Year of casting	Typology	Height	Location	Display location
1	**Francisco de Almada e Mendonça**	1885	Bust	103 cm	Prado do Repouso Cemetery, Porto	Outdoor
2	**King Afonso Henriques**	1887	Monumental Sculpture	265 cm	Paço dos Duques de Bragança, Guimarães	Outdoor
3	**St. José**	c.1922-1927	Sculpture	172 cm	MNSR, Porto	Indoor
4	**St. Joaquim**	c.1922-1927	Sculpture	174 cm	MNSR, Porto	Indoor
5	**Firmino**	c.1922-1927	Bust	64 cm	MNSR, Porto	Indoor
6	**O Pescador**	c.1922-1927	Sculpture	107 cm	MNSR, Porto	Indoor
7	**Academia – Homem Sentado**	c.1922-1927	Sculpture	88 cm	MNSR, Porto	Indoor
8	**João Marques de Oliveira**	1929	Bust	65 cm	MNSR, Porto	Outdoor

9	**Francisco Pinto Bessa**	1940	Bust	86 cm	MNSR, Porto	Indoor
10	**A Riqueza**	1954	Sculpture	140 cm	MNSR, Porto	Indoor
11	**A Música**	1957	Sculpture	137 cm	MNSR, Porto	Indoor
12	**O Trabalho**	1959	Sculpture	140 cm	MNSR, Porto	Indoor
13	**Figura Feminina**	1965	Sculpture	145 cm	Fine Arts Faculty, Porto	Outdoor

The selection of sculptures was based on the typology of the works, encompassing large-scale pieces, medium- and small-sized sculptures, as well as busts. This typological variety allows for a comprehensive comparative analysis of casting processes, corrosion patterns, and conservation needs across different sizes and complexities of sculptures. In this selection, one sculpture is large-scale (over two metres in height), eight are medium-sized (over one metre in height), and four are smaller than one metre, of which three are busts.

Secondly, the objects of study were selected based on the year of their casting. Only two of the bronze sculptures attributed to Soares dos Reis were cast during his lifetime. The remaining sculptures were cast in the 20th century, up until the 1960s, by decision of the institutions holding those pieces. This is crucial for the analysis of the metal alloys, as it allows for the identification of variations in composition over time.

Thirdly, the sculptures were selected according to their location and exposure conditions. A deliberate effort was made to include both outdoor-exposed sculptures and those preserved in controlled indoor environments.

This diversity enables a direct comparison of environmental impacts on bronze, particularly regarding corrosion processes and surface patina formation. By analysing sculptures subjected to different atmospheric conditions and maintenance regimes, it becomes possible

to assess how external factors influence the material stability and conservation strategies applicable to each context.

Environmental context plays a pivotal role in the development of surface corrosion and patinas. Sculptures exposed to polluted urban or coastal environments tend to exhibit more aggressive corrosion, whereas those in rural or indoor settings show more stable patinas and less degradation. These differences have been well documented (Chiavari et al., 2007; Robbiola & Hurtel, 1991; Scott, 2000).

In this study, four sculptures are located outdoors and nine are preserved under controlled conditions at the MNSR. This contrast offers a robust framework for comparing the effects of atmospheric exposure and preventive maintenance on long-term material stability. Moreover, six sculptures underwent detailed patina analysis, four exposed to open air and two safeguarded indoors, providing a representative cross-section for evaluating corrosion processes and conservation strategies in the Portuguese context.

3.2.1 Monumental bust of Francisco de Almada e Mendonça



Fig. 3.1 - Front and rear view of the monument to *Francisco de Almada e Mendonça* at the Prado do Repouso Cemetery in Porto, Portugal. © *Pablo General-Toro*

Historical and artistic overview

The bust of *Francisco de Almada e Mendonça* is the first sculpture by Soares dos Reis to be cast in bronze. After being modelled in 1883, it was cast in 1885 by the *Empresa Industrial Portuguesa foundry* in Amadora, Lisbon (Fig. 3.1). In addition to the bust, Soares dos Reis designed the base of the monument, which was carved in marble by the stonemason Bernardo Marques da Silva Rodrigues (M. Rodrigues, 1885a).

Located at the Prado do Repouso Cemetery in Porto, the monument has the following dimensions: 103 cm in height, 105 cm in width, and 43 cm in depth. On the back of the bust, an inscription reads:

"Fundido nas Officinas da Empreza Industrial Portugueza. Sto Amaro - Lisboa, 1885".

Cast at the offices of Empresa Industrial Portuguesa, Santo Amaro – Lisbon, 1885.

Francisco de Almada e Mendonça (1757-1804) was a prominent figure in 18th-century Portugal. He served as a Judicial Magistrate, Governor of the Porto District, and Administrator of the City Council. Born in Olivães, he died in Porto on 18 August 1804, and his remains were initially interred in the church of the Santa Casa da Misericórdia de Porto, a charitable institution (M. Rodrigues, 1885a; Soares & Lima, 1947).

In 1839, as part of a broader initiative to encourage the use of public cemeteries over traditional Catholic burial grounds, his remains were transferred to the newly inaugurated Prado do Repouso Cemetery. The solemn reinterment ceremony took place on 1 December of that year (Vasconcelos e Sousa, 1994).

Decades later, a monumental mausoleum was commissioned to honour Francisco de Almada e Mendonça. The monument was officially inaugurated on 3 September 1885, in a ceremony presided over by the Mayor of Porto, José Augusto Correia de Barros (M. Rodrigues, 1885a).

The original plaster model for the bust was initially kept by Father Alexandre Pinheiro, the main promoter of the monument. However, its current location remains unknown (Centro Artístico Portuense, 1889; Comissão Executiva dos Centenários, 1940).

Two main theories exist regarding the source Soares dos Reis used for the bust. According to Manuel Rodrigues (1885a), the sculptor based his work on a portrait of Almada e Mendonça painted by João Baptista Ribeiro in 1839, which was held at the former Porto City Hall[20] (Fig. 3.2). This interpretation is also referenced in the *Álbum Phototypico e Descriptivo das Obras de Soares dos Reis* (Centro Artistico Portuense, 1889).

[20] The research conducted by Sousa et al. (2012), published in *Os Paços do Concelho do Porto*, documents the presence of this painting since 1841. At that time, it was listed in the records of the *Secretaria do Concelho* under the title *Retrato ao natural de Francisco de Almada e Mendonça, a óleo* (no. 151). In 1868, the painting was recorded under the name *Retrato de Desembargador* (no. 599). Later, in 1872, Henrique Duarte e Sousa

Another perspective, proposed by Soares and Ferreira Lima (1947), suggests that the bust was modelled after a lithograph by Ribeiro from the same year, now housed at the MNSR[21] (Fig. 3.3). This lithograph was commissioned by Porto City Council to commemorate the transfer of Almada e Mendonça's remains to Prado do Repouso Cemetery, and it is possible that it was also based on the aforementioned painting.



Fig. 3.2



Fig. 3.3

Fig. 3.2 - Portrait of Francisco de Almada e Mendonça, formerly held at Porto City Hall. *Source: Arquivo Municipal do Porto. ID: 329968.*

Fig. 3.3 - Lithograph of Francisco de Almada e Mendonça (1839), on deposit from Porto City Hall at MNSR. *© DGPC/MNSR.*

Reis referred to it as *o retrato do corregedor e provedor da comarca do Porto, Francisco de Almada e Mendonça*.

[21] Inventory record *Francisco de Almada e Mendonça* (lithograph): 149 Lit CMP/MNSR.

The bust has been reproduced twice. In 1939, the *Comissão dos Centenários* commissioned a plaster reproduction based on a mould of the original bronze sculpture. This plaster model is now preserved at the MNSR[22] (Comissão Executiva dos Centenários, 1940). The second, a marble replica created in the 1950s, is currently displayed on the main staircase of Porto City Hall[23].

State of conservation

The bust is in reasonably good condition, although restricted access hinders detailed examination. As shown in Figure 3.1, the sculpture is located within a circular garden that is regularly maintained. However, any in-depth study requires prior permission from the *Divisão de Saúde Pública e Bem-Estar Animal* of the *Câmara Municipal do Porto*.

Structurally, the piece shows no fractures or deformations. Nonetheless, its surface exhibits a pale blue-green patina, which is more pronounced in some areas and is typical of copper corrosion in the alloy (Fig. 3.4). In rough and recessed areas, the colour ranges from dark to deep black. On the back, vertical streaks ranging from intense green to black can be seen, possibly due to leaching. Additionally, the marble pedestal exhibits traces of oxidation from leached copper ions, resulting in stains of varying green hues.

During the preliminary macroscopic observation, variations in patina texture were detected. In areas with dark corrosion, the patina was solid and well-adhered, whereas in sections with a pale green hue, it appeared powdery. The extraction of a sample from a darkened area

[22] Inventory record *bust of Francisco de Almada e Mendonça* (MNSR, plaster): 101 Esc MNSR.

[23] In the inventory carried out by Pinto (1990) of the assets of the Paço do Concelho do Porto, the marble sculpture of *Francisco de Almada e Mendonça* is listed as being made by Soares dos Reis himself. However, according to the Arquivo Histórico Municipal do Porto, this work is considered a copy of the original in bronze (Arquivo Histórico Municipal do Porto, 1964).

revealed a layer of dry green patina beneath, suggesting that this area may have been exposed to moisture.



Fig. 3.4 - Image of the bust of *Francisco de Almada e Mendonça* from four angles, illustrating corrosion issues on its surface and their effect on the pedestal. © *Pablo General-Toro*.

3.2.2 Monumental statue of King Afonso Henriques



Fig. 3.5 - *Statue of King Afonso Henriques*, in the garden in front of the *Paço de los Duques de Bragança* in Guimarães. © *Pablo General-Toro.*

Historical and artistic overview

The monumental statue in honour of *King Afonso Henriques* was commissioned from Soares dos Reis in 1884 and completed in 1887. The work was cast using the sand-casting technique at the Fundição de Massarelos foundry in Porto in that same year. The sculpture measures 265 cm in height, 114 cm in width, and 112 cm in depth.

Since its creation, the sculpture has been relocated twice. First, it was erected in the Praça de São Francisco, in the centre of Guimarães. In 1911, it was moved to the Praça do Toural, where it remained until 1941(Appendix A.1). Finally, the sculpture was taken to its current location in the gardens facing the Paço dos Duques de Bragança (Fig. 3.5). Significantly, the original pedestal was not included when it was moved for the last time; instead, a new one designed by Rogério de Azevedo was installed (Appendix A.2) (Macedo, 1943).

The sculpture's original pedestal, made of limestone, was designed by the architect José António Gaspar. Soares dos Reis specifically asked for Gaspar to be involved, as noted in a letter from May 18th, 1884 (Soares dos Reis, 1942) (Appendix A.3). Throughout the project, Gaspar played an active role, performing structural calculations and preparing a preliminary sketch. The monument's organising committee later approved this sketch.

The design of the King Afonso Henriques statue was based on thorough iconographic research of European medieval sources. The aim was to portray the monarch with historical accuracy (Arroio, 1899). Some initial sketches of the sculpture were published in the journal *Mvsev* in 1943, showing how the design developed from early ideas to the final version (Macedo, 1943). The sketch of the monument was presented to the committee, and the contract to create the sculpture was signed on September 2nd, 1885, with a budget of 7000 *reis* (M. Rodrigues, 1887b).

In the first sketches, the monarch appeared with long sleeves and a short tunic, revealing his knees, as shown in the preliminary design submitted to the committee in 1885 (Fig. 3.6). However, for the final model, the sculptor chose to make the tunic longer and the sleeves shorter. The miniature model of the sculpture was kept at the artist's home and can be seen in photographs published in the *Álbum Phototypico e Descriptivo das Obras de Soares dos Reis* (Fig. 3.7) (Centro Artistico Portuense, 1889).



Fig. 3.6 - Preliminary drawing for the monument to King Afonso Henriques, by the architect José António Gaspar, 1885. Title:PT-AMAP-RECENSEAMENTO-APP-10-2719-1_m0002. *Image courtesy of the Arquivo Municipal Alfredo Pimenta.*

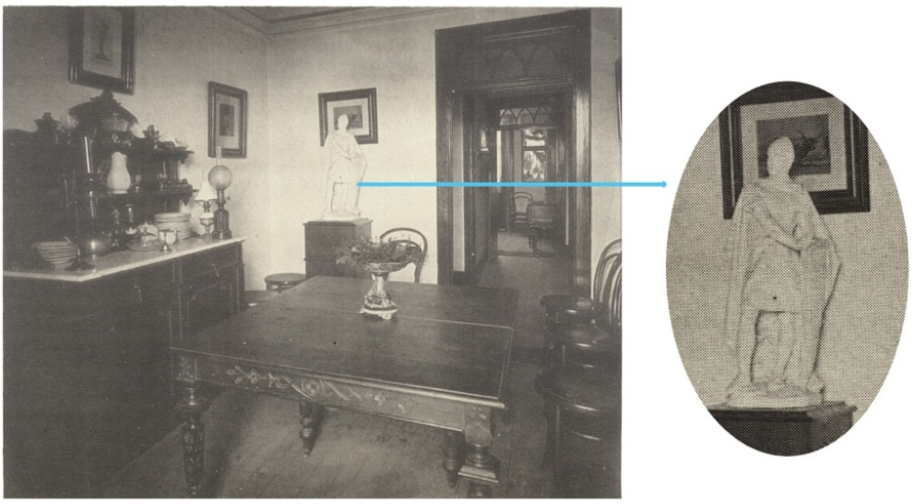


Fig. 3.7 - Interior of Soares dos Reis' house, where the plaster model of the statue of King Afonso Henriques was displayed. *Source: Álbum Phototypico e Descriptivo das Obras de Soares dos Reis, 1889, p. 41.*

In his essay about the artist, included in this album, Alves Mendes (1889) classifies the statue as academic in style. Arroyo (1899), in his analysis, suggests that the main artists involved in the sculpture were Soares dos Reis' assistants and disciples, Serafim Neves and Marques Guimarães, although the head was indeed made entirely by Soares dos Reis himself. In contrast, Macedo (1945) disagrees with Arroyo and credits Soares dos Reis as the sole technical creator of the artwork.

The plaster model considered to be the original statue of King Afonso Henriques, along with other plaster copies, is preserved at the barracks of the Monastery da Serra do Pilar, in Vila Nova de Gaia.

The statue has been copied many times. In 1940, the *Comissão Executiva dos Centenários* commissioned a plaster replica for the MNSR[24], based on the original model (Comissão Executiva dos Centenários, 1940). They also requested an iron casting of the statue's head (Macedo, 1943). Later, another iron copy was made at the *Massarelos* foundry. This copy was sent to Brazil for an exhibition and eventually placed in the former hospital of the *Associação dos Sócios da Beneficência Portuguesa* in Rio de Janeiro, where it remains today (Lacerda & Valente, 1943).

The plaster model from the MNSR was used to create the mould for the statue of *King Afonso Henrique*s in the *Castelo de S. Jorge* in Lisbon. The piece was cast in 1947 by the José de Castro Guedes foundry of Vila Nova de Gaia, under the direction of the sculptor Henrique Moreira (Moreira, 1947).

Another statue dedicated to *King Afonso Henriques* was cast in 1999 by the company *Cosme Fundição de Arte de Canelas Ltda.* and is located in the *Jardim Portas do Sol* in Santarém. This work was unveiled on March 19th, 1999. A plaster mould stored at the Monastery da Serra do Pilar was used to make it. This replica is 235 cm tall, making it thirty centimetres shorter than the original sculpture in Guimarães (I. Martins, personal communication, 4 December 2023).

[24] Inventory record statue of *D. Afonso Henriques* (MNSR, plaster): 103 Esc MNSR.

More recently, in 2016, another copy was made in artificial stone to be placed at one of the entrances to the Estádio D. Afonso Henriques in Guimarães. This version was produced by the Portuguese company Universal Rocks (Ferreira, 2016).

State of conservation

The statue consists of three main parts: the body, the sword, and the shield. A notable aspect is the transparency of the patina, both natural and artificial, on the rear, which reveals the distinct sections, cast separately, that compose the work (Fig. 3.8). Welds are observed on some of the joints, resulting from subsequent interventions, probably necessitated by degradation or relocation of the piece (Fig. 3.9 a and b). These welds are not original, since, during the period of the statue's creation, the pieces were joined using screws and mechanical adjustments through hammering, rather than through welding. In addition, small, square soldered 'windows' or patches of unknown specific function are identified, although they are presumed to be related to the hoisting of the statue onto its pedestal.



Fig. 3.8 - Detail illustrating the joint lines (indicated by arrows) between the cast sections of the statue. *Source:* General-Toro et al. (2021).



a) b)

Fig. 3.9 a, b - Identification of areas with later welds (red arrows) on the statue of King Afonso Henriques. © *Pablo General-Toro.*

The surface of the statue presents a pale green patina with variations in tone, more intense in some exposed areas. On the rear areas, the patina is darker and shows whitish areas similar to the phenomenon known as *blanching.* On the helmet, the patina is more accumulated and has a bluish tone.

In various rough areas and cavities, the sculpture exhibits dark corrosion crusts, indicative of differential corrosion processes. Surface runoff is also identified, which has caused the accumulation of greenish corrosion deposits at the base of the statue. These deposits, visible on the plinth and some lower areas of the sculpture, suggest the leaching of corrosion products over time.

3.2.3 Sculptures of S. José and S. Joaquim



Fig. 3.10 - Bronze sculptures of S. José (left) and S. Joaquim (right), held at the MNSR. ©*Pablo General-Toro, DGPC/MNSR.*

Historical and artistic overview

Although in Chapter 5 the sculptures of S. José and S. Joaquim are analysed individually, here they are presented together in their historical description. This is because they share a historical and artistic parallel: conceived by Soares dos Reis for the same purpose, cast in bronze and later incorporated into the MNSR collection simultaneously.

This pair of sculptures (Fig. 3.10), conceived in plaster by Soares dos Reis in 1880, were originally intended for reproduction in granite by a stonemason under the artist's direction. The commission originated from José Joaquim Guimarães Pestana da Silva for the chapel of his palace, situated at the corner of Rua de Almada and Gonçalo Cristóvão, in Porto (Centro Artistico Portuense, 1889).

Soares dos Reis modelled the sculptures in the Gothic style, a style widely appreciated in 19th-century Europe and found in similar examples in churches and places of worship (Comissão Executiva dos Centenários, 1940).

Soares dos Reis donated the plaster originals to the APBA, which commissioned their casting in bronze in the early 20th century. Although the sculptures bear no foundry marks, their provenance is established by the *Livro de Contas* (Account Book) of the EBAP, which managed the funds allocated for casting Soares dos Reis' work (Escola de Belas Artes do Porto, 1927). These documents detail works dispatched to the ASLF between 1922 and 1927.

In 1932, the bronze versions entered the collection of the MNSR[25], along with the original plaster models[26]. The granite versions remain *in situ* on the façade of the chapel of the Pestana Palace.

The sculpture of St. José measures 172 cm in height, 60 cm in width, and has a base of 64 cm x 33 cm. That of St. Joaquim is 174 cm in height, 60 cm in width, with a base of 63 cm x 28 cm. Both were produced using the sand-casting technique, allowing for the identification of some of their joint lines (Fig. 3.11). Notably, the pantograph points used for the granite reproduction of the plaster sculptures remain visible on the bronze pieces (Fig. 3.12), providing tangible evidence of the production process.

[25] Inventory record *St. José* (MNSR): 52 Esc MNSR. Inventory record *St. Joaquim* (MNSR): 53 Esc MNSR.

[26] Inventory record *St. José* (MNSR, plaster): 7 Esc MNSR. Inventory record *St. Joaquim* (MNSR, plaster): 8 Esc MNSR.



Fig. 3.11 - Detail of the joint lines (white arrows) on the sculpture of St. Joaquim, showing the joining of the bronze sections after the casting process, as seen in the enlarged detail. *©Pablo General-Toro, DGPC/MNSR.*

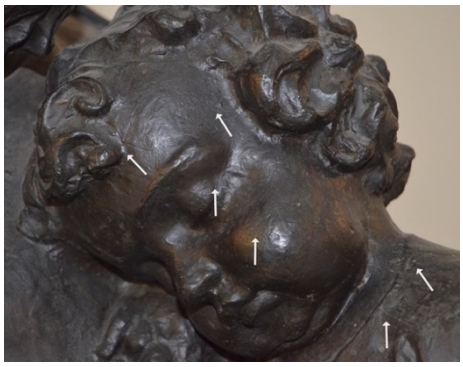


Fig. 3.12 - Detail of the face of the Baby Jesus in the sculpture of St Joseph. The pantograph marks, visible on the surface (white arrows), are preserved from the original plaster mould after the casting of the work. *©Pablo General-Toro, DGPC/MNSR.*

State of conservation

Both sculptures are in a satisfactory state of preservation, attributable to their housing in a museum environment within the MNSR since their accession to the collection. The incipient formation of a greenish patina is observed, particularly in areas of folds and recesses, susceptible to the accumulation of dust. It should be noted that, although the works formed part of the permanent exhibition until 2022, they are currently housed in the institution's store due to the museographic restructuring carried out that same year.

3.2.4 Monumental bust of João Marques de Oliveira

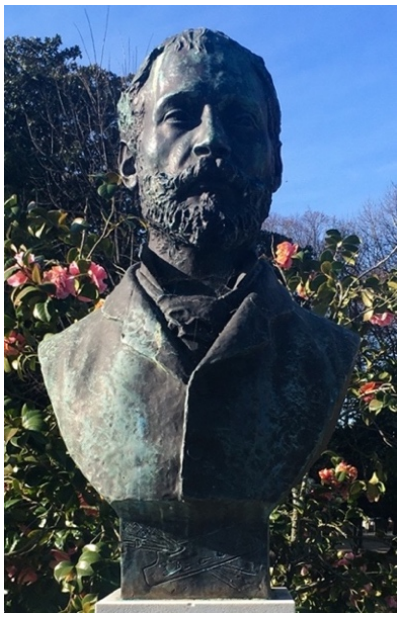


Fig. 3.13 - Monumental Bust of João Marques de Oliveira. Work by Soares dos Reis, executed in 1881 and cast in bronze in 1926. © *Pablo General-Toro.*

Historical and artistic overview

João Marques de Oliveira (Porto, 23 August 1855 – Porto, 9 October 1927) was a distinguished painter and professor who played a significant role in the Porto art scene of the late 19th and early 20th centuries. Born in Porto in 1855, he received his artistic training at APBA from 1864 to 1873. Awarded a scholarship in 1872, he travelled to Paris to further his studies under celebrated artists such as Alexandre Cabanel, Jules Lefebvre, and Benjamin Constant (Lopes, 1938).

Along with Soares dos Reis, he was a founding member of the *Centro Artístico Portuense* and the journal *A Arte Portugueza*. In 1876, he was appointed Professor of Merit at the APBA and, in 1881, interim professor. The following year, in 1882, he obtained a permanent teaching position at the same institution, where he taught Historical Drawing and Historical

Painting until the end of his career. In 1896, he was appointed Director of the Academy (Aires Silveira, n.d.).

Throughout his career, he maintained a close friendship with the sculptor Soares dos Reis. In 1881, the latter created a bust in his honour to commemorate his appointment as professor at the Academy. The bust, 65 cm high, originally belonged to Marques de Oliveira himself.

In 1926, the painter's widow commissioned the casting of the bust in bronze from the Hebrard foundry in Paris[27]. Subsequently, she ceded it for incorporation into the monument dedicated to the painter, located in the garden that bears his name in Porto. This monument was inaugurated on 11 April 1929 (Appendix A.4).

After the death of Marques de Oliveira's wife, the original plaster bust passed into the hands of his nephew, the lawyer Álvaro Roçadas. In 1940, Roçadas lent the work to be exhibited in the commemorative exhibition of Soares dos Reis, organised that same year. On that occasion, a second bronze casting was made, commissioned from the Abreu Foundry in Lisbon. This replica is currently in the MNSR[28].

In 1949, Roçadas attempted to sell the original bust to the Portuguese *Fazenda Pública* for the sum of 70,000 escudos. However, the proposal was rejected, given that other official replicas of the work already existed (Direção Geral da Fazenda Pública, 1949). Finally, in 1982, the Portuguese State acquired the original plaster piece, which is currently kept in the MNAC[29].

[27] Information obtained from the inventory record of the Marques de Oliveira bust, 96 Esc MNSR.

[28] Inventory record *bust of Marques de Oliveira* (MNSR): 96 Esc MNSR.

[29] Inventory record *bust of Marques de Oliveira* (MNAC, plaster): 2208.

State of conservation

The bust of Marques de Oliveira, including its marble pedestal, has been subjected to various acts of vandalism over time. One of the most significant occurred in April 2019, when the sculpture was spray-painted blue, with lines simulating tears on both the bust and the pedestal (Fig. 3.14). This act of vandalism appears to be linked to sporting rivalries.



Fig. 3.14 - Bust of Marques de Oliveira and pedestal, after the vandalism with blue spray paint. April 2019. © *Pablo General-Toro.*

Following the incident, the bust was cleaned by the municipal services of Porto City Council. Despite the intervention, traces of paint are still visible in some areas, although exposure to atmospheric agents has contributed to their fading.

Currently the sculpture is in good condition. It retains the original artificial patina of a dark, almost black hue. Although the formation of a natural greenish patina can be observed in

areas such as the face, hair and folds of the clothing (Fig. 3.15). Furthermore, bird droppings are visible on the surface.



Fig. 3.15 - Views of the Marques de Oliveira bust from its four sides, showing the state of preservation of its surface.

3.2.5 Figura Feminina

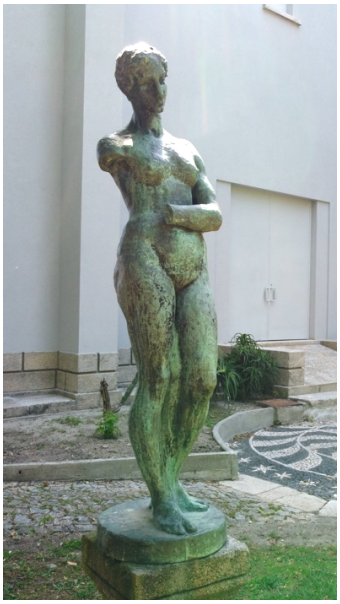


Fig. 3.16 - *Figura Feminina*, modelled by Soares dos Reis in 1867 and cast in 1965. Located in the Garden of the FBAUP. © *Pablo General-Toro.*

Historical and artistic overview

Figura Feminina (Fig. 3.16), modelled by Soares dos Reis in 1867 during his period of training at the APBA, represents a unique example within his oeuvre. Conceived as a model-mannequin for the development of other works, the sculpture features the deliberate absence of an arm. This characteristic allowed the missing arm and hand to be recreated in different positions, adapting to the requirements of each new sculpture.

Cast in 1965 by the José Castro Guedes foundry, the sculpture is currently located in the FBAUP garden. It measures 145 cm in height and 35 cm in width, with a base width also measuring 35 cm. The original plaster model is preserved in the museum of the same institution.

State of conservation

The surface of the sculpture exhibits a heterogeneous colouration, with pale green tones irregularly distributed, alternating with dark, almost black areas. Localised regions with reddish and greenish-blue hues are also visible (figs. 3.17 and 3.18).

A significant accumulation of dust and organic matter is evident in various areas of the sculpture, including vegetal remains and fragments of leaves. Bird droppings are also present, particularly on the pedestal, as well as in cavities and exposed surfaces such as the arms, shoulders, and head (figs. 3.18 and 3.19). The presence of these residues not only compromises the aesthetic legibility of the work but may also contribute to accelerated alteration processes due to their acidity and moisture-retaining capacity.

It is worth noting that no previous conservation or restoration interventions have been documented for this piece. The absence of records or visible evidence of prior treatments points to the possibility that the sculpture has not undergone systematic maintenance or specialist conservation actions, which reinforces the importance of a detailed study and the implementation of appropriate measures for its future preservation.



3.17 3.18 3.19

Fig. 3.17 - Detail of the back and arm of *Figura Feminina*, showing the various patinas on the surface. © *Pablo General-Toro.*

Fig. 3.18 - Detail of the arm-body join of *Figura Feminina*, showing the surface colouration and accumulation of plant debris. © *Pablo General-Toro.*

Fig. 3.19 - Detail of the head of *Figura Feminina*, showing the accumulation of dust, particularly noticeable on the shoulders, in the eye sockets and in the hair. © *Pablo General-Toro.*

3.2.6 Busto de Firmino



Fig. 3.20 *Busto do Firmino. © Nuno Carriço / DGPC - MNSR*

Historical and artistic overview

The *Busto de Firmino* (Fig. 3.20), created by Soares dos Reis in 1867, was modelled to compete for a state scholarship that enabled him to continue his artistic studies in Paris and Rome. The work depicts Firmino dos Santos Almeida, a student and employee of the APBA.

Between 1922 and 1927, the original plaster model was reproduced in bronze using the sand-casting technique at the foundry run by Adelino Sá Lemos, commissioned by the EBAP. The sculpture, measuring 64 x 60 x 30.5 cm, has been housed in the MNSR[30] since 1932, alongside the original plaster model[31].

[30] Inventory record *Busto de Firmino* (MNSR): 175 Esc MNSR.

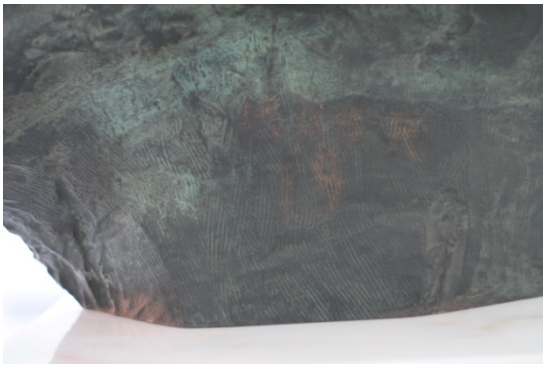
[31] Inventory record *Busto de Firmino* (MNSR, plaster): 19 Esc MNSR.

State of conservation

The bust, which is in good condition, forms part of the MNSR collection, the institution responsible for its safekeeping and preservation. At present, the piece is stored in the museum's depot. No documented information is available regarding its conservation history or any previous interventions, which underscores the relevance of its current monitoring and the detailed recording of its present condition.

Upon visual examination, green-coloured corrosion was observed on the rear part of the sculpture, specifically in the area where the bust meets the base. In the same rear area, just below this zone, remnants of a red-painted inscription reading “MNSR 19” were noted, although only partially preserved (Fig. 3.21). Additionally, similar corrosion spots were detected on the left ear and in certain areas of the curls, possibly due to the accumulation of moisture or residues.

Finally, in the chest and neck areas, yellowish corrosion was observed, accompanied by early signs of pale green corrosion, which may indicate a localised progression of surface alteration (Fig. 3.22).



Fig, 3.21



Fig. 3.22

Fig. 3.21 - Detail of the back of the bust of *Firmino*. Greenish corrosion at the junction with the base and partial remains of the red-painted inscription “MNSR 19”. © *Nuno Carriço /DGPC – MNSR.*

Fig. 3.22 - Yellowish corrosion on the chest and neck areas, with early signs of pale green corrosion. © *Nuno Carriço /DGPC – MNSR.*

3.2.7 Academia – Homem Sentado



Fig. 3.23 - Sculpture *Academia – Homem Sentado*. *© Nuno Carriço/ DGPC – MNSR.*

Historical and artistic overview

The sculpture *Academia – Homem Sentado* (Fig. 3.23) was modelled by Soares dos Reis in 1868 during his time in Paris at the studio of François Jouffroy. The original plaster model was later sent to Porto to be included in the ESBAP collection (Comissão Executiva dos Centenários, 1940).

While the MNSR sculpture inventory[32] indicates that the work was cast in bronze by order of the ESBAP before 1932, the ESBAP *Livro de Contas* for 1927 records the casting of several sculptures by Soares dos Reis without specifying the pieces in most cases (Escola de Belas Artes do Porto, 1927). Among them, it mentions the casting of a work entitled *Estudo Anatómico* carried out in 1927 for a cost of 1,800 escudos, which could correspond to

[32] Inventory record *Academia – Homem Sentado* (MNSR): 2 Esc MNSR.

Academia – Homem Sentado or another work by Soares dos Reis produced in Paris. Further research is needed to accurately determine the casting date of the sculpture.

The sculpture measures 88 cm in height x 44 cm in width, with a base of 36 cm in diameter. Currently, both the original plaster model and the bronze sculpture are housed in the MNSR.

State of conservation

The bust, which is in good condition, forms part of the MNSR collection, the institution responsible for its preservation. No documented information or visible evidence has been found to confirm any previous conservation or restoration interventions on the piece. A thin layer of superficial dust is visible across the surface, with a more noticeable build-up in certain areas.

In the section where the depicted figure is seated, particularly in areas with a rougher texture, the accumulation of dust is more pronounced. Within these deposits, localised areas of pale green corrosion can be identified in an early stage (Fig. 3.24).



Fig. 3.24 - Dust accumulation and early pale green corrosion in the rough-textured seated area of the sculpture. © *Nuno Carriço /DGPC – MNSR.*

3.2.8 O Pescador

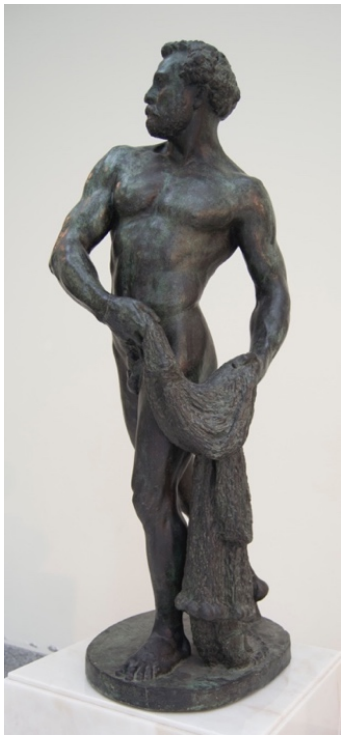


Fig. 3.25 - Sculpture *O Pescador. © Nuno Carriço /DGPC – MNSR.*

Historical and artistic overview

The sculpture *O Pescador* (Fig. 3.25) was modelled in 1870 by Soares dos Reis, already enrolled at the École Impériale des Beaux-Arts in Paris during his academic training. The work represents one of the first examples of what the artist had learned during his time in France.

The original plaster model was later transferred to the APBA, where it remained for several years. Within that institutional context, the piece was cast in bronze, although no documentation is available to precisely identify which specific works were included in the process. Only the total number of pieces cast is recorded.

The bronze sculpture became part of the MNSR collection in 1932[33], together with the original plaster model[34], where both are still preserved today (Comissão Executiva dos Centenários, 1940).

The sculpture measures 107 cm in height × 49 cm in width × 47.3 cm in depth.

State of conservation

Part of the MNSR collection, this piece exhibits a heterogeneous patina. While originally finished in a dark tone, it now displays areas of natural patina in off-white and pale green hues. These chromatic variations are especially noticeable on the front, particularly across the chest, arms, legs, and shoulders, with a marked concentration on the right shoulder. (Fig. 3.26). The presence of this patina is also evident on the pedestal and in areas of greater relief or difficult access, such as the hair and the nets, where build-up tends to occur.

Moreover, the patina extends around areas showing casting defects, notably on the wrists, the gluteal region, and the right foot (Fig. 3.27). The localised appearance of these alterations in correspondence with surface irregularities suggests the presence of a differential corrosion process in these areas, possibly influenced by specific micro-environmental conditions and the morphology of the casting defects themselves.

[33] Inventory record *O Pescador* (MNSR): 172 Esc MNSR.

[34] Inventory record *O Pescador* (MNSR, plaster): 4 Esc MNSR.

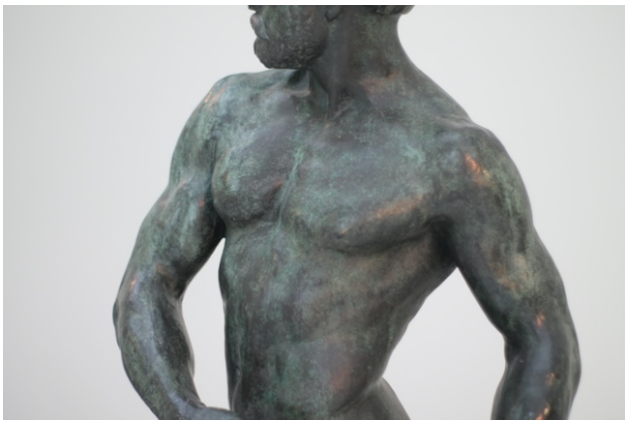


Fig. 3.26 - Detail of pale green corrosion on the torso, shoulders and arms of the sculpture *O Pescador*. *© Nuno Carriço /DGPC – MNSR.*



Fig. 3.27 - Detail of a casting defect on the right foot of the sculpture *O Pescador*. *© Nuno Carriço /DGPC – MNSR.*

3.2.9 Bust of Francisco Pinto Bessa



Fig. 3.28 - Bust of *Francisco Pinto Bessa*. © *Pablo General-Toro /DGPC – MNSR.*

Historical and artistic overview

The bust of Francisco Pinto Bessa (Fig. 3.28) corresponds to one of the bronze versions of a work originally sculpted in Carrara marble in 1878. The original marble sculpture belongs to the Porto City Council, while the plaster model is held at the MNSR[35]. The piece studied in this work corresponds to the first bronze version.

This bronze bust was cast in 1940 by the Fundição Abreu[36], commissioned by the Comissão Executiva dos Centenários on the occasion of the Soares dos Reis Exhibition held that same year at the Museu Nacional Soares dos Reis (Comissão Executiva dos Centenários, 1940).

[35] Inventory record *Francisco Pinto Bessa* (MNSR, plaster): 16 Esc MNSR.

[36] Inventory record *Francisco Pinto Bessa* (MNSR, bronze, 1940): 98 Esc MNSR.

A replica of the bust had previously been cast between 1922 and 1927, possibly at the ASLF, commissioned by the EBAP[37] (Escola de Belas Artes do Porto, 1927).

Both bronze sculptures, measuring 86 cm in height, 61 cm in width and 38 cm in depth, with a circular base of 21 cm in diameter, are currently held in the MNSR collection.

State of conservation

The sculpture, which forms part of the MNSR collection, is under the continuous care of the institution, which is responsible for its preservation and maintenance. Overall, the piece is in a stable state of conservation, with no visible structural damage.

However, early signs of pale green corrosion have been observed in localised areas on the lower part of the bust (Fig. 3.29). These alterations are associated with the accumulation of dust, particularly in certain casting pores or defects.



Fig. 3.29 - Early signs of pale green corrosion on the lower part of the bust of *Francisco Pinto Bessa*. *© Nuno Carriço /DGPC – MNSR.*

[37] Inventory record *Francisco Pinto Bessa* (MNSR, bronze, 1922-1927): 176 Esc MNSR.

3.2.10 A Riqueza



Fig. 3.30 - *A Riqueza. © Pablo General-Toro /DGPC – MNSR.*

Historical and artistic overview

A Riqueza (Fig. 3.30), modelled by Soares dos Reis in 1877, was commissioned by the stonemason António Moreira Rato, whose workshop was located in Lisbon. The work was presumably intended to be carved in stone to adorn the façade of an aristocratic residence.

In 1933, Moreira Rato's heirs attempted to sell a set of four sculptural models by Soares dos Reis to the MNSR (Moreira Rato, 1933) (Appendix A.5). Negotiations were unsuccessful. In 1938, discussions resumed, with renewed interest from the MNSR in acquiring the works (Direção Geral do Ensino Superior e das Belas Artes, 1938; Moreira Rato, 1938) (Appendix A.6 - A.7).

However, due to budgetary constraints, the pieces were ultimately sold to the MNAC, which subsequently deposited them with the MNSR (Museu Nacional Soares dos Reis, 1938) (Appendix 8).

The sculpture was cast in bronze in 1954 by the José Castro Guedes foundry in Vila Nova de Gaia, thanks to funding from the *Fundo João Chagas*, although it does not bear a founder's mark (Direcção-Geral do Ensino Superior e das Belas-Artes, 1954b). The Castro Guedes foundry was the MNSR's preferred choice for bronze casting due to the quality of its work and competitive prices (Museu Nacional Soares dos Reis, 1954b). The Abreu e Filho foundry was initially considered; however, their quotation for casting the sculpture *História* significantly exceeded that of Castro Guedes (Fundição Abreu e Filho Lda., 1954; Museu Nacional Soares dos Reis, 1954a).

The bronze sculpture measures 140 cm in height x 47 cm in width x 41.5 cm in depth. It currently forms part of the MNSR collection[38] (Museu Nacional Soares dos Reis, 1950).

Another bronze version of *A Riqueza*, cast in 1956 by the Abreu e Filho foundry in Lisbon for the Portuguese State, is exhibited at the MNAC[39]. The original plaster model was requested from the MNSR for this version (Direção Geral do Ensino Superior e das Belas Artes, 1956; P. Lapa & De Aires Silveira, 2010).

A third replica of the sculpture is located in the *Museu José Malhoa* in Caldas da Rainha[40], cast in 1959 by the José de Castro Guedes foundry, commissioned by the *Diretor de Ensino Superior e Belas Artes*.

[38] Inventory record *A Riqueza* (MNSR): 245 Esc MNSR.

[39] Inventory record *A Riqueza* (MNAC): 908 – A.

[40] Inventory record *A Riqueza* (Museu José Malhoa): Esc 116.

State of conservation

The sculpture, which forms part of the MNSR collection, is under the responsibility of this institution for its conservation and maintenance. It is currently on display in the gallery dedicated to Soares dos Reis, where it forms part of the permanent exhibition route.

The piece presents natural-looking corrosion, characterised by whitish, green, and blue-green hues. These chromatic variations are mainly located in concave areas and folds, such as those of the garment, as well as in the joints between different sculptural elements, for example, the connection between the arm and the cornucopia (Fig. 3.31).

The morphology of these areas, with pronounced relief or narrow recesses, favours the accumulation of dust, which may influence both the development and the surface appearance of the corrosion products.



Fig. 3.31 - Natural-looking corrosion, with whitish, green, and blue-green hues, located in folds and sculptural joints such as the arm and the cornucopia. © *Nuno Carriço /DGPC – MNSR.*

3.2.11 A Música



Fig. 3.32 - *A Música*. © DGPC – MNSR.

Historical and artistic overview

The sculpture *A Música* (Fig. 3.32), modelled in plaster by Soares dos Reis in 1877, was originally conceived as a model for its subsequent execution in stone. This piece is part of the group of plaster sculptures acquired by the MNAC from the firm of António Moreira Rato, a transaction already referenced in the analysis of the artwork *A Riqueza*.

An initial bronze casting of the sculpture was undertaken in 1957 by the José de Castro Guedes foundry, under the patronage of the Fundo João Chagas (Direcção-Geral do Ensino

Superior e das Belas-Artes, 1957). This bronze exemplar, with dimensions of 137 cm x 42 cm x 42 cm, is currently part of the collection of the MNSR [41].

The original plaster model is preserved at the MNAC[42], along with a second bronze version[43], cast in 1956 through state funding (P. Lapa & De Aires Silveira, 2010). A third bronze exemplar is housed at the *Museu José Malhoa*[44], the result of a casting carried out in 1959, also by the José de Castro Guedes foundry.

State of conservation

The sculpture *A Música* exhibits a notable variety of pores distributed irregularly across its surface, corresponding to imperfections generated during the casting process (Fig. 3.33). These pores are visible in different sections of the piece, both in flat areas and in morphologically more complex zones.

In various parts of the garment, as well as in recessed areas that are difficult to access, multiple points of corrosion can be observed, with chromatic variations ranging from pale green to deep green tones and more whitish areas. These corrosion spots appear in a scattered manner and are mainly located in areas where dust accumulation has been more persistent. Similar alterations are also identified on the pedestal and in the area containing Soares dos Reis's signature, likewise, associated with visible dust deposits (Fig. 3.34).

In addition, two points located on the upper part of the garment show partial loss of the artificial patina. These areas, with irregular contours, expose the underlying metal, where

[41] Inventory number *A Música* (MNSR): 262 Esc MNSR.

[42] Inventory number *A Música* (MNAC, plaster): 907.

[43] Inventory number *A Música* (MNAC): 1702.

[44] Inventory number *A Música* (Museu José Malhoa): Esc 115.

brown-coloured corrosion is visible (Fig. 3.35). This alteration is localised and does not affect other visible areas of the work.



Fig. 3.33 - Casting pores and defects visible on the surface of the sculpture *A Música*. © *Nuno Carriço /DGPC – MNSR.*

Fig. 3.34 - Corrosion spots in pale green, deep green, and whitish tones on folds and recessed areas of the garment, the pedestal, and near Soares dos Reis's signature, associated with dust accumulation. © *Nuno Carriço /DGPC – MNSR.*

Fig. 3.35 - Localised loss of artificial patina on the upper garment, revealing base metal and brown-coloured corrosion. © *Nuno Carriço /DGPC – MNSR.*

3.2.12 O Trabalho



Fig. 3.36 - *O Trabalho*. © DGPC – MNSR.

Historical and artistic overview

The sculpture *O Trabalho* (Fig. 3.36), modelled in plaster by Soares dos Reis in 1876, was commissioned by the stonemason Moreira Rato. This work forms part of the group of pieces sold in 1938 to the MNAC by Rato's descendants, as part of an acquisition that enabled the museum to incorporate several academic and commemorative models associated with the sculptor. The piece is currently on deposit at the MNSR[45], where it was placed on loan.

The bronze version of the sculpture, measuring 140 cm in height, 52 cm in width, and 51.5 cm in depth, was cast in 1959 at the José de Castro Guedes foundry. This process was carried out under the patronage of the Fundo João Chagas (Direcção-Geral do Ensino Superior e das

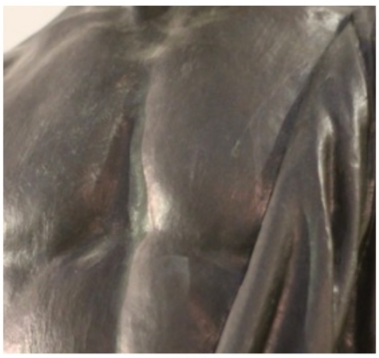
[45] Inventory number *O Trabalho* (MNSR, plaster): 87 Esc MNSR.

Belas-Artes, 1959). At present, this bronze version is part of the MNSR's permanent collection[46].

State of conservation

The sculpture is held in the collection of the MNSR, the institution responsible for its long-term preservation and maintenance. As part of the museum's holdings, the piece is subject to regular monitoring to assess its material condition.

Upon visual examination, areas showing early signs of pale, blue and dark green corrosion have been identified, particularly on the chest and in recessed zones of the surface (Fig. 3.37, 3.38, 3.39). These areas coincide with sections where dust accumulation is more evident. In some cases, the corrosion appears in droplet or streak-like formations (Fig. 3.39), possibly resulting from the contact of an unidentified liquid with the surface of the sculpture.



3.37



3.38



3.39

Fig. 3.37 - Pale green corrosion on the chest of the sculpture *O Trabalho*. *© Nuno Carriço /DGPC – MNSR.*

Fig. 3.38. Blue-green and dark green corrosion in recessed areas of the sculpture *O Trabalho*. *© Nuno Carriço /DGPC – MNSR.*

Fig. 3.39 - Detail of dark corrosion, blue-green corrosion in recessed areas, and corrosion in droplet and streak-like formations on the sculpture *O Trabalho*. *© Nuno Carriço /DGPC – MNSR.*

[46] Inventory number *O Trabalho* (MNSR): 299 Esc MNSR.

3.3 INSTITUTIONAL BRONZE CASTING AND PRESERVATION OF SOARES DOS REIS'S SCULPTURE

"Tal é o mármore em que o nos transmite a parte mais sublime do seu peregrino espirito e urge que elle seja apeado do sitio onde se acha no cemitério de Agramonte, exposto as intempéries do nosso húmido e tão variável clima, e carinhosamente o abriguem, para que se não diga que não soubemos conservar ao paiz essa joia de incomparável valor. Que lhe substituam uma copia, de mármore ou de bronze, feita aqui ou lá fora, que para isso ainda o gesso existe na Academia das Bellas Artes; mas que esse augusto symbolo estético dos mais fecundos sentimentos humanos não se perca para sempre" [sic].

"Such is the marble in which he conveys to us the most sublime part of his remarkable spirit, and it is imperative that it be removed from its current location in the Agramonte Cemetery, exposed to the elements of our humid and highly variable climate, and lovingly sheltered, so that it cannot be said we failed to preserve this jewel of incomparable value for the nation. Let it be replaced with a replica, in marble or bronze, made here or abroad, for the plaster cast still exists at the Academy of Fine Arts; but let this august aesthetic symbol of the most profound human sentiments not be lost forever."

In this text, written by António Arroio for the magazine *Ocidente* (1939), the conservation state of the marble statue of *Conde de Ferreira*, originally located in Agramonte Cemetery, was highlighted, alongside the urgent need to relocate it to an indoor space. Today, the original work by Soares dos Reis is preserved at the MNSR, while a bronze replica, commissioned by the EBAP before 1927, was placed in its original location in the cemetery in 1943.

Throughout the 20th century, several years after the death of Soares dos Reis, significant efforts were undertaken to preserve the artist's work. Much of it was created in plaster, a remarkably fragile and deterioration-prone material, making its conservation a considerable challenge due to the risk of permanent loss. These official initiatives, driven by both public

and private institutions, were crucial in preventing the disappearance of a significant portion of the sculptor's artistic legacy, ensuring its protection and transmission to future generations.

It is important to distinguish between works that were replicated after the artist's death and those bronze pieces executed during Soares dos Reis's lifetime. While they do not belong to the former group, these works, possibly cast under the direct supervision of the artist, include the bust of Francisco de Almada e Mendonça (1885) and the monument to King Afonso Henriques (1887).

3.3.1 Sculptures Cast During Soares dos Reis's Lifetime

3.3.1.1 Bust of Francisco de Almada e Mendonça

The first of these works is the bust of Francisco de Almada e Mendonça, conceived in 1883 and cast in 1885 by the *Empresa Industrial Portuguesa* in Lisbon. This bust is part of a funerary monument erected in honour of Almada e Mendonça (described in section 3.1.1). The idea for this monument originated in 1866, when Raimundo Joaquim Martins, a member of Porto City Council, proposed the construction of a mausoleum (Vasconcelos e Sousa, 1994). However, the project did not come to fruition until the 1880s, when Father Alexandre Pinheiro, then director of Agramonte Cemetery, organised a fundraising campaign for its construction.

3.3.1.2 Sculpture of King Afonso Henriques

The initiative for the creation of the monumental statue of *King Afonso Henriques* began as a local project in Guimarães, aimed at commemorating Portugal's first king in his birthplace. Over time, the proposal grew in scope, evolving into a project of national and international significance (Câmara Municipal de Guimarães, 1882). A key element in this process was the significant contribution from the Portuguese community in Brazil, which provided the majority of the donations required to complete the work. To advance this initiative, committees were established both in Brazil[47] and Portugal[48] (Gazeta de Noticias, 1882a, 1882b; M. Rodrigues, 1885b) to coordinate fundraising efforts. Support was sought from municipalities, banks, businesses, and other organisations to gather the necessary donations. Additionally, various public events, such as theatrical performances and bazaars, were organised and contributed significantly to the fundraising campaign[49] (Commisão Vimaranense do Monumento a D. Afonso Henriques, 1883; Ferreira de Mello, 1882).

When Soares dos Reis was invited to participate in the project for the monumental statue of the *King Afonso Henriques* in 1884, the final material for the work had not yet been decided. Consultations were held with prominent members of Vimaranese society to determine which material would best suit the vision of the monument. Although marble was initially considered a more economical option, its acquisition required importing blocks from the Carrara quarries in Italy, which significantly increased costs due to transportation (Soares dos Reis, 1884).

[47] The Brazilian committee was established on 29 October 1882, chaired by the Count of S. Salvador de Matosinhos.

[48] The Portuguese committee was established on 15 November 1882, chaired by the then Mayor of Guimarães, António Coelho da Motta Prego.

[49] These initiatives raised a total of 11.924.930 reis for the project.

Ultimately, it was unanimously decided that bronze would be the most suitable material. This choice, in addition to being more practical economically, ensured greater durability and conferred prestige on the work.

Regarding the foundry site, the *Fundição do Arsenal* of Lisbon was initially considered. However, due to the high cost quoted by this institution and the impossibility of carrying out the casting abroad, as the bronze had been donated by the Portuguese State, it was decided to conduct the process in Porto (Appendix A.9) (Soares dos Reis, 1885b).

3.3.2 Sculptures cast after the death of Soares dos Reis

3.3.2.1 Sculptures cast by the Valmor Legacy

The first sculpture by Soares dos Reis to undergo casting after the artist's death was the bust titled *O Negro* (1873), cast in 1904. The casting was commissioned from the Fonderie Thiébaut Frères in Paris (Academia Real de Belas Artes de Lisboa, 1901). Despite this, the sculpture was cast by the Gasné Foundry, to which the Thiébaut Foundry was sold in 1901 (Musée d'Orsay, 2023).

The casting of the bust *O Negro* was made possible thanks to the Viscount of Valmor's bequest, for which 515 francs (99,395 réis) were paid. This bequest was established in 1901 and granted the Royal Academy of Fine Arts of Lisbon a sum of 70,000 réis, to be managed in a fund whose proceeds would be used to acquire Portuguese and foreign artworks for the National Museum of Fine Arts in Lisbon (Academia Real de Belas Artes de Lisboa, 1901).

Among other works of art, part of the Count of Almedina's collection was acquired through this bequest, including Soares dos Reis' sculpture *Mocidade*, which appears to correspond

to the sculpture *Filha dos Condes de Almedina*. This piece was purchased for 2,000 réis (Academia Real de Belas Artes de Lisboa, 1901).

Thanks to the Valmor Bequest, a series of reforms were also implemented, that reorganised the Academy of Fine Arts of Lisbon, as well as the School and Museum of Fine Arts, known as Janelas Verdes. However, the equivalent institutions in Porto were excluded from this project (J. Figueiredo, 1901).

The Valmor Bequest continued to sponsor initiatives until the second half of the 1920s, although its impact gradually diminished over the years due to currency depreciation (Baião, 2019). In 1982, the Valmor Bequest was merged with the Lisbon Municipal Architecture Prize.

The bust of the *Viscountess of Moser* (1882), incorporated in 1922, is also housed in this museum. The piece was cast by order of the State, although the foundry of origin is not specified.

3.3.2.2 Sculpture cast by the Academia Portuense de Belas Artes

At the end of the first decade of the 20th century, the APBA expressed concern about the conservation state of the monumental marble statue of the *Conde de Ferreira* (1876), one of António Soares dos Reis' most iconic works, located in the Agramonte Cemetery in Porto. The statue's exposure to climatic and environmental conditions had begun to deteriorate it, prompting the consideration of preservation measures.

To protect the original, it was proposed to replace the marble statue with a bronze replica. For this purpose, the Portuguese Parliament was petitioned to grant the material needed for casting. In *Projeto de Lei 19-D*, dated 23 November 1911, the Parliament approved the allocation of the requested bronze. However, this decision was later revoked on 3 August 1912, and instead, a subsidy of 800,000 réis was granted, corresponding to the budget estimated by ASLF for the production of the new bronze statue (Pádua Correia, 1911).

3.3.2.3 Sculptures cast by the Escola de Belas Artes do Porto

The EBAP, which was responsible for preserving and safeguarding much of Soares dos Reis' artistic legacy at the time (see Table 3.2), played a key role in organising the casting of his sculptures. Under the direction of Henrique António Guedes de Oliveira, the EBAP requested the necessary resources from the Lisbon authorities to proceed with the casting of the sculptures (Escola de Belas Artes do Porto, 1920).

Table 3.2 List of Sculptures Cast by Commission of the School of Fine Arts of Porto, Prior to 1927. (ASLF: Adelino Sá Lemos Foundry)

Name	Creation	Casting	Foundry	Localisation
Busto de Firmino	1867	Pre 1927	Unknown (ASLF?)	MNSR
Academia - homem sentado	1868	1927	ASLF	MNSR
Negro sobre uma placa	1869	Pre 1927	Unknown (ASLF?)	MNSR
O Pescador	1870	Pre 1927	ASLF	MNSR
Busto de Domingos de Almeida Ribeiro	1876	Pre 1927	Unknown (ASLF?)	MNSR
Cabeça do Conde de Ferreira	1876	1926	ASLF	MNSR
Saudade	1878	Pre 1927	ASLF	MNSR - Museu José Malhoa
Busto de Francisco Pinto Bessa	1878	Pre 1927	Unknown (ASLF?)	MNSR
S. Joaquim	1880	Pre 1927	ASLF	MNSR
S. José	1880	Pre 1927	ASLF	MNSR

Narciso	1881	Pre 1927	ASLF	MNSR
Busto de Joaquim Pinto Leite	1881	Pre 1927	Unknown (ASLF?)	MNSR
Busto de Hintze Ribeiro	1884	Pre 1927	Unknown (ASLF?)	MNSR
Medallion of Augusto Cândido Ramos	1884	Pre 1927	Unknown (ASLF?)	MNSR
Busto da Inglesa Mrs. Leech	1887	Pre 1927	Unknown (ASLF?)	MNSR

Prior to this, the director had requested a quote from the ASLF, which was issued on 24 December 1920. This document detailed the proposal for casting several sculptures, including *São Joaquim*, *São José*, *O Pescador*, an *Academia*, five different busts, the medallion of *Augusto Cândido Ramos*, and the bust of *Correia de Barros*. The total estimated cost for producing these pieces was twelve thousand escudos (Sá Lemos, 1920b) (Appendix A.10).

According to a letter sent by Director Guedes de Oliveira to the Director General of Fine Arts, the works that the EBAP intended to cast in bronze were:

"[...] estátua de S. José; ídem de S. Joaquim, ambas de tamanho natural; O Pescador; uma Academia; cinco bustos diferentes; o baixo relevo da Morte de Adonis; bem como medalhão Augusto Cândido Ramos e busto Correia de Barros, estes dois últimos, obtidos a solicitações minhas para o caso de serem fundidos é com a respectiva instalação, de catorze contos e duzentos escudos (Guedes de Oliveira, 1921).

"[…] the sculpture of *São José*; likewise, *São Joaquim*, both life-sized; *O Pescador*; an *Academia*; five different busts; the bas-relief *Death of Adonis*; as well as the medallion *Augusto Cândido Ramos* and the bust of *Correia de Barros*. The latter two, obtained at my request, were intended for casting, with the corresponding setup costing fourteen contos and two hundred escudos."

It is important to highlight that the piece *Death of Adonis* was not included in the budget submitted by Sá Lemos but was listed among the works to be cast, as compiled by the EBAP. The sculptures by Soares dos Reis mentioned in this request were, at that time, housed in the Soares dos Reis Museum, which was then located in the Monastery of São Lazaro, now the Porto Municipal Public Library.

With the support of the then Director General of Fine Arts, Augusto Gil, an initial allocation of eight thousand escudos was secured for the bronze casting of the sculptures. This amount was gradually increased through additional grants of two thousand escudos, ultimately reaching a total of fifteen thousand escudos (Gil, 1921).

Between 1922 and 1927, the institution continued commissioning the casting of the artist's works. The records from EBAP's account book for that period document a series of payments related to this process (Escola de Belas Artes do Porto, 1927):

On 30 June 1922, EBAP made a payment of 7,000 escudos to the ASLF for works that had already been cast and delivered. The records do not specify the author of the pieces subjected to casting.

On 11 May 1925, another payment of 3,000 escudos was made to the same foundry, and on this occasion, it was explicitly stated that the cast works were by Soares dos Reis. However, no information is provided regarding which specific works were cast in bronze.

On 6 January 1926, EBAP made a payment of 1,000 escudos to the ASLF for casting the head of the statue of *Conde de Ferreira*. Additionally, on 30 March of the same year, a payment of 2,000 réis was recorded for casting the bust of *Dr Correia de Barros* and other works. On 15 May 1926, 200 escudos were paid for casting the bas-relief of *Augusto Cândido Ramos*.

On 20 May 1927, EBAP made a payment of 1,800 escudos to the same foundry for moulding the sculpture titled *Estudo Anatómico*.

It is significant that, unlike the other works, the sculpture *Narcissus*, which is not specifically listed among the pieces by Soares dos Reis commissioned for casting by EBAP or recorded in the MNSR inventory, bears the stamp of the ASLF.

3.3.2.4 Sculptures cast by the Comissão Executiva dos Centenários

In *1938*, during a session held on *20 January*, the *Comissão Executiva das Comemorações Centenárias do Mundo Português*, known as the *Comissão dos Centenários*, agreed to organise an event in honour of *Soares dos Reis* by exhibiting his works. This initiative was part of a broader set of celebrations promoted by the Comissão dos Centenários itself, which had been established that same year to coordinate a series of commemorative activities marking the 800th anniversary of Portugal's foundation (1140) and the 300th anniversary of its Restoration (1640), both of which took place in 1940.

In this context, the *Exhibition of the Artworks of Soares dos Reis* was part of a series of highly significant cultural events, including the *Exhibition of the Primitives*, organised by the *Museu Nacional de Arte Antiga (MNAA)*; the exhibition of *Portuguese goldsmithing* from the *16th and 17th centuries*, held in *Coimbra*; and the *Comparative Sculpture* exhibition, hosted at the *Palace of Mafra*. For the organisation of these exhibitions, the participation of the National Academy of Fine Arts of Portugal was requested as a co-organising entity.

From the *initial conception* of this exhibition, the importance of preserving *Soares dos Reis'* artistic legacy was emphasised. The *Minutes of the Comissão dos Centenários* particularly highlighted the urgency of protecting several of his artworks, many of which were at significant risk of deterioration.

"[...] Uma grande exposição no Porto da obra de Soares dos Reis que é preciso reunir, inventariar, estudar e salvar, fundindo em bronze alguns dos gêssos [sic] que estão a perder-se." (Comissão Executiva dos Centenários, 1938).

"[…] A major exhibition in Porto of the works of Soares dos Reis, which must be gathered, inventoried, studied, and preserved, casting in bronze some of the plaster pieces that are being lost."

Among the artist's artworks, plaster sculptures, bronze pieces with casting defects, and marble works damaged by prolonged exposure to the elements were identified (Comissão Executiva dos Centenários, 1940). This concern reflected a broader commitment to preserving the national artistic heritage at a key moment of reaffirmation of Portuguese cultural identity.

As a result of this initiative, contracts were signed with the Abreu Foundry in Lisbon for the casting of some pieces, including sculptures, busts, and medallions (See table 3.3). These works were cast using the lost-wax technique and are now housed in the MNSR, except for the statue of *Conde de Ferreira*, which has been on deposit at the José Malhoa Museum in Caldas da Rainha since 1949.

Table 3.3 Sculptures cast by order of the *Comissão Executiva dos Centenários* for the exhibition of Soares dos Reis' work, held at the MNSR in 1940.

Name	Creation	Casting	Foundry	Localisation
Busto de Domingos de Almeida Ribeiro	1876	1940	Fundição Abreu	MNSR
Conde de Ferreira	1876	1940	Fundição Abreu	MNSR - Museu José Malhoa
Busto de Francisco Pinto Bessa	1878	1940	Fundição Abreu	MNSR
Busto do pintor Marques de Oliveira	1881	1940	Fundição Abreu	MNSR
Busto de Joaquim Pinto Leite	1881	1940	Fundição Abreu	MNSR
Filha dos Condes de Almedina	1882	1940	Fundição Abreu	Sent to Brazil?

Busto da Viscondessa de Moser	1883	1940	Fundição Abreu	MNSR
Medallion of José Simões de Almeida	1884	1940	Fundição Abreu	MNSR
Carpideira (sketch)	?	1940	Fundição Abreu	MNSR

In addition to the aforementioned sculptures, a plaster replica of the bust of Francisco de Almada e Mendonca was created, which is housed in the MNSR, as well as a replica of the bust of Emília das Neves, preserved at the National Theatre Museum in Lisbon.

3.3.2.5 Sculptures cast with support from the João Chagas Bequest

João Pinheiro Chagas was a prominent politician and Portuguese Ambassador to France, born in Rio de Janeiro in 1863 and passing away in Lisbon in 1925. In 1941, his wife, Maria Teresa Chagas, donated the proceeds from the sale of a property located on Avenida de Nice, in Estoril, to the Portuguese State, following its auction by the government. The resulting funds were used to establish the João Chagas Fund, specifically intended to benefit the MNSR. This fund was created to support both the acquisition of artworks and the enrichment of the museum's library (Garrett Pinho, 2014).

During the 1950s, thanks to the João Chagas Fund, new castings of several works by Soares dos Reis were carried out, including key pieces such as sketches, figures, and the artist's death mask, which had been made in plaster by Teixeira Lopes Senior (Barata Feyo & Van Zeller, 1960; M. F. Figueiredo & Van Zeller, 1961).

The sculpture *História* was chosen as the first work by Soares dos Reis to be cast during that decade. The Directorate-General for Higher Education and Fine Arts required that at least three specialised foundries be consulted for this task. However, the then-director of the Soares dos Reis National Museum (MNSR), Salvador Barata Feyo, only requested quotes

from two foundries: the Abreu Foundry in Oeiras, Lisbon, and the José de Castro Guedes Foundry in Vila Nova de Gaia. Barata Feyo explained that a third company was not consulted because only these two met the necessary conditions to carry out the casting of the sculpture properly (Barata Feyo, 1954d; Direcção-Geral do Ensino Superior e das Belas-Artes, 1954a).

The Abreu Foundry submitted an estimate of 36,000 escudos for the casting of the sculpture *História*, a sum that the MNSR director considered excessive (Barata Feyo, 1954a, 1954b; Fundição Abreu e Filho Lda., 1954). In contrast, the José Castro Guedes Foundry offered a quote of 30,000 escudos for casting four sculptures by Soares dos Reis: *História* (10,000 escudos), *Riqueza* (10,000 escudos), *Saudade* (5,000 escudos), and *Cristo* (5,000 escudos). This latter estimate was ultimately accepted (Barata Feyo, 1954c).

In November 1955, the Minister of National Education, Francisco de Paula Leite Pinto, visited the MNSR. During his visit, he ordered the bronze casting of several sculptures by Soares dos Reis, which had until then been in plaster and required a more durable medium. The MNSR proposed casting six of the artist's pieces, including the busts of *Fontes Pereira de Melo*[50], *Hintze Ribeiro*[51], and *Emília das Neves*, as well as the sculptures *A Música* and the models *Náufrago* and *O Tempo*. Additionally, the work *Ismael* by Augusto Santos was included in the list.

As with the sculptures cast in 1954, a quote was requested from the José Castro Guedes Foundry. The following estimates were provided: 4,500 escudos for the bust of *Fontes Pereira de Melo*, 3,500 escudos for the bust of *Hintze Ribeiro*, and 5,000 escudos for that of *Emília das Neves*. The casting of *A Música* was estimated at 8,000 escudos, while the models

[50] The bust of *Fontes Pereira de Melo* was deposited at the MNSR in 1939 by the Porto Commercial Association, at the request of the museum's then-director, Vasco Valente (De Oliveira Calem, 1939). A replica of this bust, cast prior to 1938, is currently displayed on the upper floor of the Porto Commercial Association's Palace, positioned at the top of the grand staircase. The foundry responsible for the casting remains unidentified, as the bust lacks any foundry marks.

[51] The plaster bust of Hintze Ribeiro was donated by the EBAP to the newly inaugurated MNSR in 1920.(Escola de Belas Artes do Porto, 1920).

Náufrago and *O Tempo* were quoted at 700 and 2,800 escudos, respectively (Barata Feyo, 1955).

3.3.2.6 Sculpture cast by the Escola Superior de Belas Artes do Porto

The casting of the sculpture *Figura Feminina* was part of an initiative promoted by the ESBAP during the second half of the 1960s, aimed at conserving and preserving its artistic collection. This project encompassed various actions, including the conservation and restoration of paintings, sculptures, and frames.

In the area of sculpture, the ESBAP selected several pieces created by its students over the years, originally preserved in plaster, to be cast in bronze. This initiative, like those previously mentioned, sought to safeguard the most artistically significant pieces by ensuring their durability using a more resilient material.

The casting of this sculpture was commissioned from the José Castro Guedes Foundry, which undertook the casting of at least six sculptures as part of this initiative.

Among these pieces was the sculpture *Figura Feminina*, cast in 1965. The cost associated with the casting of this work amounted to 6,000 escudos, financed through that year's annual budget under the category "Extraordinary Promotion of Pedagogical, Cultural, and Scientific Activities" of the Ministry of National Education (Escola Superior de Belas Artes do Porto, 1966).

3.4 LEGAL FRAMEWORK OF SCULPTURAL REPRODUCTION AND COPYRIGHT: FROM THE INTERNATIONAL CONTEXT TO THE CASE OF SOARES DOS REIS

The reproduction of sculptures, particularly those that have achieved public renown, has been a recurring practice throughout the history of art. This phenomenon has not only enabled the preservation of iconic works but has also facilitated their dissemination across different eras and cultural contexts.

Notable examples of this practice can be found in sculptures created millennia ago that have survived to the present day. In Ancient Greece, such works were replicated in marble by contemporaries of the original artists. Later, the Romans, admirers of these pieces, acquired them as spoils of war during their military campaigns. These masterful copies from antiquity were highly valued by Roman patrons, who favoured them over contemporary creations, which were considered to be of inferior quality (Marvin, 1997).

Despite this assertion, the creation of a Roman replica of an ancient masterpiece required not only manual skill but also the artistic judgement of the replicator, without the aid of mechanical techniques. These pieces typically bore the craftsman's signature rather than that of the original author, highlighting the existence of specialists in the production of replicas, who achieved significant recognition and prestige in their craft (Marvin, 1997).

During the Renaissance and Baroque periods, Greek masterpieces and their Roman replicas, recovered from ruins, were reproduced and restored to meet the growing interest in Antiquity. Classical sculpture became an artistic and philosophical model, symbolising the cultural values of the Renaissance. This renewed appreciation spurred the production of reproductions, created using techniques such as prints and drawings, which gained great popularity as decorative items associated with refined taste (Postle, 1997).

For example, during the Baroque period, Gian Lorenzo Bernini operated a workshop where restorations were carried out, directly intervening on sculptures from Antiquity. One of the

sculptures restored in his workshop was the *Sleeping Ariadne*, created between 150 and 175 AD, which belonged to the collection of Queen Christina of Sweden and is now housed in the Prado Museum in Madrid (Museo Nacional del Prado & Schröder, 1994).

Technological advancements in the 19th century marked a turning point in the democratisation of sculpture, making it accessible to a wider audience. Discoveries made during the 1830s played a crucial role in this process. The invention of machines capable of altering the dimensions of a sculpture, such as the *Moulding Physiotype*[52] and the *Artistic Reducer*[53] patented by Frédéric Sauvage, along with the *mechanical reduction*[54] method patented by Achille Collas in 1836, enabled the mass production of sculptural works, transforming their dissemination and reach.

The growing demand for reproductions of popular sculptures gave rise to a highly competitive market dominated by a few specialised foundries. Companies such as Christofle, Siot-Decauville, and the renowned Barbedienne, the latter in collaboration with Achille Collas, worked closely with artists to produce editions of their works. These foundries diversified their offerings by presenting variations in scale, materials, and prices, allowing them to cater to a broad and diverse audience (M. R. Figueiredo, 1992; McWilliam, 1997).

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[52] The *Physionomètre*, later known as the *Physionotype Mouleur* (Moulding Physiotype), was a portable instrument designed to accurately capture the reliefs and contours of objects or facial profiles. It consisted of a metal box with a movable core made up of steel pins that adjusted to the pressure exerted by the object being reproduced. Through a solidification system using tallow and hot water, the device created rigid hollow models, which were useful for moulding, drawing, modelling, or sculpting with precision. This innovative apparatus enabled significant advancements in the artistic and technical reproduction of three-dimensional forms. (Berr, 1881).

[53] The *Artistic Reducer* was a device based on the pantograph that allowed sculptures to be reduced to any scale with proportional precision (Berr, 1881).

[54] The mechanical reduction method was a system based on a three-dimensional process that enabled the reduction of sculptures and reliefs to a smaller scale with high precision (Europeana; DMG-Lib.org, 2013).

This process of reproduction of sculptures continued throughout the 20th century, leading to the proliferation of editions in a wide range of materials. While bronze, plaster, and terracotta remained predominant choices, more affordable materials, such as zinc and lead, began to be used (M. R. Figueiredo, 1992; Gazda, 1995). These metals, being easier to work with and having significantly lower melting points than bronze, facilitated mass production and significantly reduced manufacturing costs.

The reproduction of sculptures was not always conducted legally, and unauthorised copies negatively impacted both the artists and the quality of the works. As Figueiredo (1992) notes, abuses in this field were already documented. In the 18th century, renowned sculptors such as Falconet, Houdon, and Clodion suffered financial losses due to copies made by forgers and imitators who reproduced their works without permission. These practices undermined the artists' income and eroded the exclusivity and prestige of their creations.

In the long term, illegal reproductions not only harmed the creators but also altered the perception of sculptural art. The proliferation of systematic copies and pastiches, though popular with the public, contributed to the vulgarisation of the original models. This phenomenon intensified in the second half of the 19th century. As mass production began prioritising quantity over quality, it gradually diminished the artistic and cultural value of reproductions. This shift also blurred the boundary between art and commodity.

The market for illegal copies of artworks has long posed a challenge to copyright and intellectual property protection, dating back to the 19th century. The case of Auguste Rodin is a prominent example that highlights the need for stricter regulations in this field. In 1916, the artist donated his works to the French State, setting a unique precedent that allowed the government to regulate the production of new editions of his sculptures. According to Decree No. 93-163 of 1993, the Musée Rodin holds the exclusive right to produce original bronze editions using the plaster moulds from its collection. These editions are strictly limited in number, in accordance with the *Code de la Propriété Intellectuelle*, and are considered originals only if numbered from 1/8 to 8/8, along with the artist's proofs marked with Roman numerals from I/IV to IV/IV (Décret n°93-163 du 2 février 1993, 1993).

Any piece that does not meet these criteria, such as the reproductions sold in the museum shop, is classified as a reproduction and is not recognised as an original work. To ensure transparency and avoid confusion in the market, must bear a visible stamp on the sculpture indicating their status as reproductions. This stamp serves as a crucial measure to protect both collectors and the artist's legacy, clearly distinguishing original works from copies and safeguarding the authenticity and value of the originals (Musée Rodin, n.d.).

Under current French legislation, the protection of sculptures is not limited solely to the work of Auguste Rodin but extends to all sculptures cast in France. The regulations specify that sculptures are considered original if their production is limited to a maximum of eight numbered copies, properly stamped on the surface of the piece. Furthermore, to be recognised as originals, these pieces must have been produced under the direct supervision of the artist or the rights holders of the work of art (Décret N°95-172 Du 17 Février 1995 (France), 1995).

3.4.1 Copyright Law in Portugal

Copyright protection laws in Portugal date back to the first half of the 19th century. The first legislation on the protection of production rights was proposed on 21 February 1827 and published in *Gazeta de Lisboa* No. 45. This law did not mention sculptors. According to Article 1, it granted the author of any written work, musical composition, painting, or drawing exclusive rights to their creations, extendable to their heirs for a period of ten years after their death throughout the Kingdom of Portugal. This term was extended to 60 years if the work belonged to a corporation or society established by law (Art. 2) (Proposta de Lei Sobre o Privilegio Dos Authores, Ou Editores de Obras Impressas, Lithografadas Ou Gravadas, 1827).

Subsequently, a new copyright law was introduced through the Decree of 8 July 1851, known as the *Lei da Propriedade Litteraria*. This legislation expanded copyright protection

to other artistic fields, including sculpture. The proposal that led to this decree was presented by Almeida Garrett in 1839 and was initially approved by the Chamber of Deputies in 1841, although it was not published at the time. Later, after revisions, the project was approved by the Parliament and promulgated in 1851 (Lei de Propriedade Litteraria, 1851).

This law granted authors rights over their works for the duration of their lifetime, including the ability to reproduce them and authorise their reproduction, with no limit on the number of reproductions (Title III, Art. 18). After the author's death, the rights to their artworks were transferred to their successors for a period of 30 years. In the case of posthumous works, the successors retained rights over them for 30 years following their publication (Title I, Arts. 1–4).

The author, or their representatives, had the right to transfer their artworks' rights, in whole or in part, to third parties for a period deemed appropriate, even while retaining ownership of the physical artwork (Title I, Art. 5 and Title III, Art. 19). However, this principle did not apply when the author sold the artwork: in such cases, copyright was transferred to the purchaser, unless an explicit clause stated otherwise (Title III, Art. 19).

Furthermore, the law stipulated that the Portuguese State held rights to literary, scientific, and artistic works commissioned by it. These rights extended for a period of 30 years from the date of the artwork's publication (Title I, Art. 6).

The 1851 Decree was replaced by the *Código Civil Portuguez* of 1867, approved by Royal Charter on 1 July of that year. In this code, the provisions relating to non-literary artistic works are found in Articles 602 to 606 (*Codigo Civil Portuguez 1867*, 1868). The 1867 law provided more specific and detailed protection for the rights of creators of artistic works (Art. 602), which were regulated in the same manner as the rights of authors of literary works (Arts. 570 to 593).

The 1867 Civil Code was the legislation in force during the lifetime of Soares dos Reis, guaranteeing him rights over his works. This framework remained in effect until 1927, when Portugal adopted the provisions of the Berne Convention (1886), which it had joined in 1911.

Like its predecessor, the 1867 law granted the author exclusive rights over the reproduction of their works (Title III, Chapter 2, Section III, Art. 602). In the case of artistic works, including sculpture (mentioned as *moldagem*), these had to be submitted and registered with the Academy of Fine Arts of Lisbon, with the option to provide copies of the original drawings of the artworks[55]. The Academy, in turn, was required to publish these records in the *Folha Oficial* (Title III, Chapter 2, Section IV, Arts. 604.2 and 605). This registration system confirmed the author's ownership of the artistic work, granting them the corresponding rights and protecting them from potential fraud and false attribution.

In this context, the law clearly penalised the production and publication of works without the author's consent. The sanctions included the confiscation of unauthorised copies and payment to the author of an amount equivalent to the value of the copies sold. Furthermore, those who reproduced works fraudulently were held liable for any financial losses suffered by the author (Title III, Chapter 2, Section V, Arts. 607 and 612).

Regarding copyright after the author's death, the *Código Civil Portuguez* stipulates that these rights remain with the author's successors, representatives, or those to whom the artist had transferred their rights, for up to 50 years after the author's death. Similar to the 1851 law, the state and public institutions that had commissioned a work from the author retained these rights for 50 years following its publication.

In the 20th century, Portugal's accession to the Berne Convention on 29 March 1911 marked a significant shift in the country's copyright regulations. This international treaty, originally adopted in 1886, established uniform copyright protection among member countries.

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[55] Artigo 604º §2º: "*Se a obra for de lithographia, gravura ou moldagem, ou versar sobre alguma destas artes, a entrega e o registo serão feitos, pela mesma fórma, na Academia de Bellas artes de Lisboa. Neste caso, porém, o auctor poderá substituir o deposito dos dous exemplares pelo dos desenhos originaes."*
"If the work is a lithography, engraving, or moulding, or pertains to any of these arts, the submission and registration shall likewise be carried out at the Academy of Fine Arts of Lisbon. In this case, however, the author may substitute the deposit of two copies with that of the original drawings."

In Portugal, the first major revision of copyright law, which until then was part of the *Código Civil Portuguez* of 1867, occurred in 1927. This change involved adopting the provisions of the Berne Convention through the enactment of the *Regime de Propriedade Literária, Científica e Artística*, published on 27 May of that year (Carvalho Maia, 1927). The new law expanded protection to artistic creations, specifically including sculpture, as noted in Section E of Article 2 of the legal text.

The *Regime de Propriedade Literária, Científica e Artística* not only extended copyright protection to various forms of artistic creation but also introduced specific provisions regarding the reproduction and publication of artistic works.

Article 3 states that, in addition to the literary and artistic expressions mentioned in Article 2, reproductions of original works are also protected by copyright. This means that, in the realm of sculpture, any reproduction of an original piece, even if involving changes in size or aesthetic details, remains under the intellectual ownership of the original author, not the creator of the reproduction, as outlined in Article 13. This principle reinforces the protection of the original author against unauthorised uses of their artwork.

Similarly, Article 8§2 provides a more precise definition of publication in relation to artistic pieces. This regulation considers the date of publication of an artistic work to correspond to one of two possible moments: the first public exhibition of the piece or the delivery of the work to the person who commissioned its creation.

The 1927 law also introduced important provisions regarding the transfer of copyright. According to this legislation, copyright was perpetually transferable to the author's descendants, who could, in turn, transfer it to third parties, either freely or through a paid transaction (Art. 15 and Art. 15§1). This measure ensured the continuity of the economic rights associated with the artworks, even after the creator's death.

However, this perpetual transfer of rights was subject to the legal status of the artwork in question. Using the case of sculptor Soares dos Reis as an example, the law specified that these perpetual rights were applicable only if the protected artwork had not entered the public

domain at the time the decree came into effect. Since Soares dos Reis had passed away 38 years before the promulgation of this law, his creations were still under copyright protection, and legal ownership remained with the artist's family.

A significant feature of the 1927 law is its treatment of collaborators in the creation of an artistic work. According to this legislation, any assistant or individual who contributed to the creative process through critiques, amendments, or retouching should not be recognised as a collaborator or co-author of the work, unless such participation was explicitly authorised or acknowledged by the principal author (Art. 21§3).

Throughout the legal history of copyright up to 1927, significant transformations in copyright laws can be observed, particularly regarding the duration of work protection. Some of these laws share several similarities, such as those enacted in 1867 and 1927. However, one of the main differences between these two regulations lies in the length of time copyright remains with the author and their descendants. Under the 1851 law, copyright protection was limited to 30 years, while the 1867 law extended this period to 50 years. In contrast, the 1927 law granted perpetual copyright protection.

An important change was introduced with the enactment of Decree-Law 46978 on 27 April 1966, which reinstated that the rights of the author and their descendants over a work would remain valid for 50 years after the author's death (Art. 25) (Decreto-Lei nº 46980, de 27 de abril, 1966). This provision remained in effect with Decree-Law No. 63/85 of 14 March 1985 (Art. 35), which reaffirmed this duration for copyright protection (Decreto-Lei n.º 63/85 de 14 de Março, 1985).

However, in 1997, a significant amendment to the 1985 Decree-Law was introduced to align with European Economic Community legislation. This amendment was implemented under Directive 93/98/EEC of 29 October, which aimed to harmonise copyright regulations among member states (Decreto-lei n.º 334/97 (Portugal), 1997). As a result of this reform, the duration of copyright protection was extended to 70 years after the author's death, in line with European standards, a term that remains in effect to this day.

3.4.2 Reproductions of Soares dos Reis' artwork

Although António Soares dos Reis was recognised in artistic and cultural circles during his lifetime, his work did not achieve significant popular appreciation during that period or in the years immediately following his death. Many of his pieces, excluding public monuments, were private commissions, as evidenced by the large number of busts he produced.

After his passing, artists who knew him played a key role in promoting his recognition. Notable initiatives include the publication of the *Álbum Phototípico* of Soares dos Reis' artworks in 1889, reissued in 1988, and the monument in his honour created by Teixeira Lopes in 1904, located near his birthplace.

With the opening of the first foundries in Portugal, Soares dos Reis' work began to be officially reproduced in bronze. The ASLF collaborated with the ESBAP, while the EATL reproduced sculptures and models by the artist. These pieces are now housed in private collections and public institutions, including the MNSR and the Casa-Museu Teixeira Lopes, located next to the building that once housed the foundry of the same name.

Among the works reproduced by the Teixeira Lopes Foundry are the bust *Flor Agreste* and *Ms Elisa Leech* (reduced version), the model of *Cristo Agonizante*, the study of *Cristo Morto*, whose final version was made in polychromed wood, the bas-relief *Morte de Adonis*, the sculpture *O Abandonado*, the sketches for the statues of *King Afonso Henriques* and *Avelar Brotero*, as well as the sketches for *A Filha dos Condes de Almedina*, *Tanagra*, *Eco*, and the medallion of Amelia de Macedo (Valente, 1940).

The original clay models mentioned earlier, some of which are currently housed in the MNSR, have had various owners over time. For instance, the sketch of *Avelar Brotero* and the medallion of *Amelia de Macedo* belonged to Diogo José de Macedo, while the sketch of *A Filha dos Condes de Almedina* was owned by Alfredo da Cunha. One of the clay sketches of *Tanagra* was in the possession of Dr João Barreira, whereas other pieces, such as *Caridade*, *A Tigela Partida*, and *Figurita*, belonged to Arnaldo Neves, and *Saudade* to D.

Maria de Santiago. This information, along with an inventory of Soares dos Reis' artworks, was compiled by Diogo de Macedo, then a member of the National Academy of Fine Arts, and sent to the director of the MNSR, Vasco Valente (Lino, 1938).

Among the most well-known and reproduced sculptures by António Soares dos Reis are the bust of the Englishwoman *Ms Leech* and, notably, the bust titled *Flor Agreste*.

An illustrative document on the history of the latter sculpture is the book *A Flor Agreste. Era uma vez uma escultura…*, published in conjunction with the itinerant exhibition of the same name. This exhibition took place between July and October 1986 at the MNSR.

The bust of *Flor Agreste* was carved in marble by António Soares dos Reis in 1881. That same year, it was purchased by Maria Francisca Archer for 250,000 réis, remaining in the possession of the Archer family until 1932. In that year, it was announced for auction on 29 October at the Silva Porto salon (Pereira Viana, 1986).

Considering this situation, on 27 October, two days before the auction, writer Aarão de Lacerda informed the Council of the ESBAP about the imminent sale. In response, the council decided to send a telegram to the Minister of Education, requesting the purchase of the bust to be donated to the MNSR (Escola de Belas Artes do Porto, 1920).

The bust was eventually purchased by the Porto City Council and, in 1939, became part of the MNSR collections following the transfer of the Porto Municipal Museum's holdings to the institution.

One possible reason for the popularity of the *Flor Agreste* sculpture among the public lies in the authorisation that permitted the reproduction of this and other artworks by Soares dos Reis in plaster. According to Pereira Viana (1986), the reproduction rights for the artist's sculptures were granted by Amélia de Macedo, Soares dos Reis' widow, who still held the rights to her late husband's artworks. Amélia de Macedo authorised the reproduction of these pieces to the *Renascença Portuguesa* Association, which, in turn, commissioned the Casa

Baganha, renowned for its expertise in plasterwork, to reproduce some of the artist's sculptures.

In a 1996 interview conducted by Maria Natália Lobo with economist and professor Manuel Duarte Baganha (1922–2004) for her master's thesis (Lobo, 1998), it was mentioned that António Enes Baganha, founder and first owner of Casa Baganha, a company specialising in stuccos and plaster, had a contract granting him the right to reproduce Soares dos Reis' artworks in plaster. In this context, the interviewee recalled that moulds for the bas-relief *A Morte de Adonis* (The death of Adonis) were kept in the office of Casa Baganha, located on Rua do Rosário in Porto. Thanks to this agreement, some reproductions of Soares dos Reis' sculptures reached the Faria Guimarães School (later renamed Soares dos Reis), where António Enes Baganha taught until his death in 1934.

In the 1920s, the ASLF published a catalogue featuring reproductions of sculptures by prominent Portuguese artists, such as Soares dos Reis and António Teixeira Lopes. In the case of Soares dos Reis, whose artistic legacy was managed by his heirs, it is plausible that the production of these pieces was authorised by his wife, although no documentary records explicitly confirming such authorisation have been identified to date. On the other hand, the sculptures of António Teixeira Lopes, also featured in the catalogue, present a different context, as the sculptor was alive at the time and actively producing new pieces. This suggests that explicit authorisation from Teixeira Lopes himself would have been required for the ASLF to reproduce his artworks.

The increase in the number of reproductions of António Soares dos Reis' artworks is a phenomenon whose cause remains uncertain. However, since the earliest reproductions in plaster and bronze, the production of these pieces has risen significantly. Over time, reproductions were no longer confined to these supports but began to incorporate new materials such as terracotta - sometimes polychromed-, ceramics, and synthetic resins (*marfinite*). A notable example of this evolution is the reproduction of the *Flor Agreste* sculpture in biscuit porcelain, undertaken as part of the 200th-anniversary celebrations of the Vista Alegre ceramics factory.

The reproduction of Soares dos Reis' artworks was not limited to the ASLF and Casa Baganha but also involved other foundries such as Guedes e Ribeiro, Castro e Guedes, and José da Silva Abreu. Some of the moulds used in these processes are still preserved in foundries that remain operational.

Bronze reproductions gained significant presence in the market, both through direct sales and auctions, where they continue to be offered to this day. This large volume of available pieces has led to recurring questions about the authenticity of many of them.

An example of this concern within society is a letter sent by businessman and producer Carlos Cudell Goetz (1959) to the then-director of the MNSR, Salvador Barata Feyo. In the letter, Cudell mentions three small bronze pieces, all signed by Soares dos Reis, including reduced versions of the bust *Ms Leech*, *Flor Agreste*, and a female sketch (possibly *Tanagra*), the latter bearing the mark of the Castro e Guedes Foundry.

In his correspondence, Cudell expresses scepticism regarding the authenticity of these works, describing them as "common bronzes" and requesting information from the museum director about how many of these reproductions might be on the market. He also raises doubts about whether these pieces were produced during the sculptor's lifetime or, alternatively, were reproductions made later.

In response to this letter, Salvador Barata Feyo confirmed that the pieces observed at the antique shop were "modern copies." He also noted the existence of a significant number of such reproductions (Barata Feyo, 1959).

Today, reproductions of António Soares dos Reis' artworks are easy to find in a variety of contexts. In the Porto area, these pieces have been identified in second-hand bookshops, private libraries, house-museums, various shops, and even restaurants, becoming notably integrated into every day and cultural spaces.

However, the availability of these reproductions in physical antique shops has significantly declined in recent years, shifting progressively to the digital market. On popular online stores

and platforms in Portugal, notable examples include the busts *Flor Agreste* and *Ms Leech*, offered in materials such as plaster, bronze, biscuit porcelain, and synthetic resin. Additionally, these reproductions remain common in auction houses, where iconic works like *Flor Agreste*, *O Abandonado*, and *Cristo Crucificado* are frequently sold, both in full-size and reduced versions. Most of these pieces, crafted in materials such as plaster, bronze, and marble, are offered at Portuguese auctions, sometimes reaching values exceeding one thousand euros, particularly in the bronze and marble versions (Invaluable.com, n.d.).

The reproduction of António Soares dos Reis' artwork outside official channels highlights the tensions between artistic dissemination, heritage control, and market dynamics. While authorised reproductions of his sculptures played a crucial role in preserving and popularising his legacy, the existence of pieces produced without official oversight or outside agreements with the artist's heirs has raised questions about the authenticity and quality of many of these works.

Examples such as bronze copies identified in auction houses and online sales platforms, or the proliferation of reproductions in various materials such as terracotta, ceramics, biscuit porcelain, and synthetic resins, demonstrate how Soares dos Reis' artwork has been appropriated by a less regulated market. This market does not always guarantee fidelity to the artist's original intentions, or the technical standards of the companies initially authorised to reproduce his sculptures.

However, this period of widespread popularity for Soares dos Reis' work, reproduced outside official channels, has also been appreciated from a historical perspective. One example is the MNSR's initiative to collect a set of the various reproductions of *Flor Agreste* made throughout the 20th century, recognising that these copies serve as a clear testament to the cultural impact of this artwork during that time, consolidating its presence in both every day and institutional contexts.



Fig. 3.40 - José Abreu retouching a bronze reproduction of the *Flor Agreste* sculpture after its casting in his workshops. Photograph by Orlando Miranda, published in *Boletim Amigos de Gaia*, No. 10, May 1981.

3.5 FINAL REMARKS ON CHAPTER 3

The analysis of Soares dos Reis's bronze sculptures has made it possible to identify a representative group of works and to place them within the institutional and legal contexts that shaped their reproduction throughout the 20th century in Portugal. This approach considers both historical dimensions and contemporary regulatory frameworks. The selection is not based solely on material criteria, but reflects the contexts in which these sculptures were reproduced and the purposes behind such initiatives.

The study of these practices highlights how the works were reproduced to reinforce a shared national identity, to confirm the artistic consecration of Soares dos Reis. It also ensured their material preservation through more stable copies, given the progressive deterioration of the original plaster models, a particularly fragile support.

This chapter brings to a close the section dedicated to the patrimonial and institutional dimensions of bronze sculpture. The research now shifts its focus to technical and material aspects, addressing specific challenges within the field of conservation.

PART II SCIENTIFIC CHARACTERISATION AND THE STUDY OF MATERIALS AND CORROSION IN THE BRONZE SCULPTURES OF ANTÓNIO SOARES DOS REIS

CHAPTER 4. AN ANALYTICAL STUDY OF MATERIALS AND CORROSION IN BRONZE SCULPTURES. AN OVERVIEW

4.1 INTRODUCTION

Understanding the materiality of copper alloy sculptures is essential to their conservation. Beyond the technical dimension, scientific analysis of these works allows for the reconstruction of manufacturing processes, the identification of material transformations, and the assessment of deterioration risks. In this context, conservation increasingly depends on scientific knowledge as the foundation for ethical and sustainable decision-making.

Analytical studies have shown that the long-term stability of copper alloys depends not only on their chemical composition, but also on environmental conditions and the history of previous interventions. Understanding these interrelated factors requires the application of diverse analytical techniques, which in this study range from non-invasive methods, such as X-ray fluorescence spectroscopy (EDXRF), to more advanced approaches. Among these, X-ray diffraction (XRD) provides structural information about corrosion compounds. Microscopy techniques, including optical microscopy and scanning electron microscopy

combined with energy-dispersive X-ray spectroscopy (SEM-EDS), allow for detailed surface and compositional analysis.

Together, these methods are essential for perceiving the technological characteristics of the alloys and, at the same time, for distinguishing between stable, protective patinas and active corrosion processes; a distinction that is fundamental for making informed and responsible conservation decisions.

Within this framework, it is important to consider how methodological approaches have developed across different countries, shaped by diverse technical traditions, heritage priorities, and facilities constraints. While countries such as Italy, France, and the United States have produced a robust and extensive corpus of research on copper alloy sculpture, the Portuguese context has evolved more selectively, often focusing on urban interventions and targeted conservation projects.

This study, through the analytical examination of a work by António Soares dos Reis, seeks to contribute to a field that remains underdeveloped in Portugal. Its integration into a structured scientific investigation not only aims to deepen technical knowledge of casting practices and corrosion dynamics in the national context, but also provides original Portuguese data to the international corpus, thereby strengthening the dialogue between science and the conservation of modern sculptural heritage.

4.2 SCIENTIFIC APPROACHES TO THE STUDY OF COPPER ALLOYS IN HERITAGE OBJECTS

4.2.1 Historical overview of copper alloy analysis methods

The systematic analysis of alloys in controlled environments has historical precedents dating back to the Middle Ages, when cupellation was used to determine the proportion of noble metals such as gold and silver (Rehren and Eckstein, 2002, as cited in Hsu & Martinón-Torres, 2019). Rooted in prehistory, this method facilitated the extraction and refining of metals. It involved separating those more reactive to oxygen (such as copper and lead) from less reactive metals.

The term *cupellation* derives from *cupel*, a porous vessel made of refractory material capable of withstanding high temperatures. During the process, the impure metal was placed in the cupel and exposed to a stream of hot air in a specialised furnace. Impurities (such as copper, tin, and lead) would oxidise, either volatilising or being absorbed by the refractory material, while gold or silver remained in an almost pure state (Britannica, 2019). The study of copper alloys has played a pivotal role in both archaeometallurgy and heritage conservation. In archaeological contexts, it has enabled the identification of manufacturing techniques and the composition of ancient objects. In conservation, its analysis is essential for the preservation of sculptures and other heritage assets, as well as for the development of materials with comparable properties for restoration and the reproduction of historical pieces. Throughout history, copper and its main alloys, such as bronze (copper-tin) and brass (copper-zinc), have played a central role in the production of utensils, weapons, tools, and decorative elements in various civilizations.

With the advancement of science, particularly during the 18th century, the analysis of these materials became increasingly reliant on more systematic and precise chemical methods. This period marked a turning point in the development of analytical techniques, enabling a

detailed examination of the properties and compositions of metal alloys. In this context, a tradition of meticulous studies in the field of archaeological metallurgy emerged, laying the foundations for advanced research in the 19th and 20th centuries. A documentary project that embodies this historiographical tradition is FLAME (Flow of Ancient Metals Across Eurasia) [56], led by the School of Archaeology at the University of Oxford. It functions as a curated archive of metallurgical analyses, compiling published data from around 300 articles dated between 1790 and 1869, along with nearly 750 from later periods (Perucchetti et al., 2021).

According to Pollard (2013), gravimetric methods[57] were primarily used to determine the proportion of elements such as copper and tin in archaeological alloys in the 18th century and early 19th century. Other methods included fusion and blowpipe testing, chemical precipitation to separate minor elements (e.g., arsenic), controlled oxidation to separate copper from tin, density measurements, colour change observation, and magnetism tests to detect iron.

In the second half of the 18th century, some of the earliest analytical studies of metals were conducted. One of the pioneering examples was the work of Michel Jean Jerome Dizé (1754–1852), who analysed ancient coins (Greek, Roman, and Gallic) and published his results in 1790. Additionally, Dizé investigated creating copper alloys with arsenic to assess the resulting physicochemical characteristics. The understanding of chemical elements also advanced significantly during this century (M. Pollard, 2013).

[56] Link to the FLAME Project: https://flame.arch.ox.ac.uk/index.html#home

[57] The gravimetric method is a quantitative chemical analysis procedure that determines the concentration of a specific component in a sample by converting it into a substance of known composition that can be separated and weighed. This method involves preparing a solution, isolating the desired component using techniques such as precipitation or electrodeposition, drying the precipitate, and finally calculating its quantity based on the obtained weight.

In 1789, Antoine Lavoisier (1743–1794) published a classification of 31 elements (including copper), organised according to their atomic weight and chemical properties. Lavoisier divided the elements into four categories: basic elements (gases), metals, non-metals, and earths. This system, which laid the foundations for the future periodic table, culminated in 1869 with Dmitri Mendeleev's (1834–1907) reorganisation of the elements. Mendeleev himself even predicted the existence of yet undiscovered elements, such as gallium, scandium, and germanium, which were subsequently identified in 1875, 1879, and 1886, respectively (Guharay, 2021; Marshall, 2019).

Since the second half of the 19th century, the study of alloys, particularly copper-based ones, reached a high level of development, establishing itself as a key field in scientific research and industrial applications. This progress was largely driven by the technological advancements of the Industrial Revolution, which encouraged the exploration of new metal combinations with enhanced properties. As a result, alloys such as bronze and brass became essential for manufacturing mechanical components, tools, and industrial structures.

Similarly, analytical methods experienced significant advancements. From the 1870s onwards, gravimetric methods achieved high levels of precision due to innovations in sample preparation, the use of specific reagents, and optimising techniques such as precipitation and electrodeposition (M. Pollard, 2022).

Regarding studying the physical characteristics of copper alloys, an article in *Nature* by Rose (1896) highlighted significant advances in researching copper-zinc alloys by Georges Charpy (1865–1945), known for his contributions to studying the mechanical properties of metals, including the pendulum that bears his name[58]. Charpy investigated how heat treatment, specifically exposure to constant temperatures over prolonged periods, affected

[58] The Charpy pendulum is a device used to determine a material's brittleness or resistance (toughness) to fracture. This test involves subjecting a specimen to a controlled impact from the pendulum, recording the energy absorbed during the material's fracture. The absorbed energy, which corresponds to the area under the load curve at the moment of impact, is known as resilience. This method provides a measure of the material's ability to withstand sudden deformations or fractures under dynamic loading conditions.

the microstructural and mechanical properties of brass. This process, which involved transforming crystalline phases, demonstrated that small variations in temperature could significantly alter the alloy's strength, hardness, and ductility. The conclusions of these studies were particularly beneficial to the industry, as they enabled the optimisation of copper-zinc alloys for specific applications.

In early studies of alloys, optical microscopy (OM) played a fundamental role in observing and identifying crystalline phases, as well as detecting defects and structural pathologies that alloys may develop when exposed to different environments. This technique has enabled researchers to analyse the morphology of metallic materials and understand the mechanisms affecting their stability and behaviour under various environmental conditions (Rosenhain, 1909). Complementarily, since the 19th century, metallography has been a fundamental tool in studying metal alloys, allowing for characterisation of a metal's microstructure through detailed observation of its internal structure, composition, and spatial distribution of grains, inclusions, and phases (Scott, 1991).

The analysis of metals took a qualitative leap in the first half of the 20th century with the introduction of commercial spectrometers[59], such as UV-Visible and infrared spectrophotometers. According to Thomas (1991), these instruments facilitated analysing electronic transitions and identifying elements in metallic materials. Pollard (2022) highlights that these advancements revolutionised archaeometallurgy, enabling more detailed and efficient characterisations of ancient alloys. The introduction of spectrometers represented a significant advancement by reducing the amount of metallic sample required for analysis. Instead of large volumes, small shavings obtained with fine drill bits were sufficient, greatly improving previous techniques. However, today, even these minimal

[59] Spectrometers are devices that analyse how a substance interacts with light by breaking it down into its different colours or wavelengths. This technique helps identify the elements present in a sample by observing how they absorb or emit energy in the form of light (Thomas, 1991).

extractions are considered unacceptable, with a strong preference for non-invasive methods to ensure the preservation of historical heritage.

The development of non-invasive methods for metal analysis intensified after World War II, driven by techniques based on the interaction of radiation (neutrons, electrons, X-rays, gamma rays, and infrared) with matter. The introduction of portable equipment, such as Raman spectroscopy, Fourier-transform infrared spectroscopy (FTIR), and energy dispersive X-ray fluorescence (EDXRF), in the late 20th century has enabled the analysis of large or difficult-to-transport objects, providing quick and reliable results without compromising the integrity of heritage artefacts. This study details, in Chapter 5, the application of the EDXRF technique to determine the metallic composition of the artworks analysed in this research, highlighting its advantages for *in situ* analysis.

4.2.2 Corrosion and patina in copper alloys: evolution of scientific insight and conservation relevance

Driven by the natural tendency of metals to return to their original mineral state, corrosion is a chemical or electrochemical process that occurs on a metal surface when it comes into contact with the environment. This process reflects the metals' pursuit of thermodynamic stability by reducing their energy potential. Metals, extracted from minerals and ores through refining and extraction processes, are brought to a higher energy state, making them susceptible to corrosion over time (Javaherdashti, 2008; Revie & Uhlig, 2008).

From a materials perspective, ISO 8044, issued by the International Organization for Standardisation ISO (2020), defines corrosion as the *"physicochemical interaction between a metal and its environment, resulting in changes to the metal's properties, which may lead to significant deterioration of the metal's function, the environment, or the technical system of which they are a part."* In the corrosion of both copper and alloys in which this metal is the primary component, the dissolution of copper metal ions occurs, a process known as

decuprification. In an aqueous solution, copper oxidises, transitioning to Cu (I) or Cu (II). Cu (I) is slightly soluble in water, meaning that the cuprite (Cu_2O) film that forms on the surface is insoluble.

According to the Swedish National Council for Nuclear Waste (Kärnavfallsrådet) (2009), in a pure, oxygen-free aqueous environment, the corrosion reaction of copper is: $2Cu(s) + H_2O \leftrightarrow Cu_2O + H_2$. The situation changes if decuprification occurs in the presence of complexing agents, which form soluble complexes due to their chemical properties. For example, in the presence of Cl^-, the solubility of Cu (I) increases (Zhou & Ogle, 2018). In this regard, distinguishing between active corrosion processes that lead to rapid metal dissolution those that result in the formation of stable, protective layers of corrosion products —patina— is essential for conserving copper alloy sculptures, as each process affects the material's stability and appearance in different ways.

Patina is frequently known as the insoluble surface layer that forms on the metal's surface as a result of complex chemical reactions involved in its natural oxidation. Influenced by equilibrium with its surroundings, visually manifesting in changes in colour and texture. Both naturally formed and arrifically induced patinas provides partial protection against environmental factors (Bernardi, Chiavari, et al., 2009; Bureš et al., 2019; Chiavari et al., 2006, 2007; Dermaj et al., 2007; Hemning, 1977; Mills, 1990; Weil, 1977).

In low-pollution or indoor environments, it develops as a thin and compact film, resisting aggressive agents. Since Antiquity, patina has been regarded as a noble element, valued for its beauty and symbolism, reflecting the passage of time in sculptural artworks (L'héronde et al., 2019). In such environments, patina formation can take between ten and thirty years, during which the metal surface undergoes various phases of transformation (Graedel et al., 1987; Knotkova & Kreislova, 2007).

In highly contaminated environments, such as polluted atmospheres or in the presence of particular aggressive agents like chlorides, corrosion processes can lead to significant metal degradation, potentially compromising the structural integrity of the material. The formation of a stable patina acting as a protective barrier in highly unlikely, as active corrosion

processes produces compounds that progressively deteriorate the underlying metal (Edwards et al., 2023). In copper and its alloys, corrosion typically begins through electrochemical processes, forming a thin layer of reaction products, such as salts, on the surface, facilitated by cycles of moisture and dryness (Knotkova & Kreislova, 2007).

Several factors influence the rate and severity of corrosion in copper alloys. Among the most influential environmental factors are temperature and humidity, whose combination can either accelerate or, in some cases, slow down the corrosion process. For instance, moisture and dryness cycles play a crucial role: during periods of high humidity, hygroscopic compounds present on the alloy surface dissolve upon exceeding a critical threshold, facilitating chemical reactions that accelerate corrosion products formation. Studies have shown that these cycles induce more aggressive corrosion behaviour. The material's properties also influence the rate and severity of corrosion (Aastrup et al., 2000; Fonseca et al., 2004; Strandberg & Johansson, 1997; Watanabe et al., 2002).

The concentration of reactive agents in the environment, such as sulphur dioxide (SO_2), hydrogen sulphide (H_2S), ammonia (NH_3), and nitrogen dioxide (NO_2), is a key factor in the corrosion of copper alloys. In industrialised environments, these pollutants can generate particularly aggressive products that compromise the stability of copper and its alloys. Meanwhile, in marine environments, the deposition of sodium chloride (NaCl) promotes a distinct type of corrosion. In this regard, studies have shown that when humidity exceeds 75% and combines with high levels of these agents, the corrosion process accelerates significantly, affecting not only copper but also other components present in the alloys (Lopez Badilla et al., 2010; Revie & Uhlig, 2008).

Similarly, erosion and mechanical stress on the surface of the alloy can contribute to the removal of protective layers, continuously exposing the material to conditions that promote corrosion (Dermaj et al., 2007; Knotkova & Kreislova, 2007).

The systematic study of patina and corrosion began in the 18th century with the first observations on the natural oxidation of copper in different atmospheric and aquatic environments. Researchers such as Antoine Baumé (1773), François-Antoine Foucroy

(1786), Joseph Louis Proust (1799), Thomas Thompson (1802), and John Murray (1806) made pioneering contributions by describing the processes of metal alteration (Baumé, 1773; Foucroy, 1789; Murray, 1809; Riederer, 1995; T. Thompson, 1810; Fournier, 2012). These early studies were largely qualitative, relying on visual observations and basic chemical tests. While valuable for their time, they lacked the sensitivity and specificity of later analytical methods.

In 1825, John Davy conducted one of the first comprehensive studies on patina in archaeological bronzes, analysing pieces from various sites (Corfu, Kastrades, Ithaca, and Samos). The scientist used wet chemical analysis to identify compounds such as cuprous oxide, basic copper carbonates, copper trihydroxychlorides, and cassiterite (Davy, 1833; Scott, 2002). Later, Michel-Eugène Chevreul and Marcelin Berthelot further explored the relationship between patina appearance, alloy composition, and environmental agents by studying bronze statuettes found in the Temple of Serapis in Egypt (Chevreul, 1856; Berthelot, 1894).

Wet analytical techniques are a quantitative method for mineral analysis, in which the sample is dissolved in a suitable liquid medium, such as an acid, allowing its decomposition. Until 1947, wet analytical methods, including colorimetry, volumetric analysis, and gravimetric analysis[60], were the most commonly used techniques for identifying and quantifying corrosion products (Servicio Geológico Mexicano, 2017).

The intense industrial activities that emerged with the Industrial Revolution marked a turning point in the composition of urban and industrial environments, leading to significant environmental variations and a sharp increase in pollution levels in areas where copper alloy

[60] Colorimetry determines the concentration of a substance by measuring the intensity of the colour produced by a specific chemical reaction. Volumetric analysis quantifies a component by precisely measuring the volume of a reagent of known concentration that reacts completely with the sample. Gravimetric analysis, on the other hand, is based on determining the amount of an analyte by converting it into an insoluble compound, followed by its separation and weighing. (Servicio Geológico Mexicano, 2017).

sculptures are located. This drastic change has affected the stability of existing patinas, altering the chemical characteristics that once ensured the preservation and durability of these artworks. The increased burning of fossil fuels, particularly coal, released large quantities of SO_2 into the atmosphere, leading to a shift in the dominant corrosion products from oxides and carbonates to sulphates (Chiavari et al., 2007; Robbiola, Fiaud, & Pennec, 1993; Weil et al., 1982).

According to Weil (1977), these transformations have altered the properties of natural patinas, which were originally thin, compact, and translucent, with reddish or brown tones. However, the increasing presence of sulphur compounds in the environment has led to the formation of green or mottled black patinas, reflecting an accelerated deterioration process linked to industrial pollution.

As early as the 1860s, a progressive darkening of the patina on copper alloy sculptures was observed, sparking growing interest in determining the causes of this phenomenon. In response to this concern, a commission was established in Germany specifically to investigate the issue by installing purpose-cast busts exposed to various atmospheric conditions in the streets of Berlin. The aim was to systematically analyse the factors responsible for the alteration and degradation of the patina’s original appearance (Riederer, 1995).

W.H.J. Vernon's pioneering work in the early 20th century established the interplay between alloy composition and environmental factors in copper alloy corrosion, using controlled laboratory experiments, a methodological advancement. His research on zinc-copper alloys (brasses) showed that initial corrosion depended on copper content, but long-term corrosion was dominated by pollutants affecting zinc-rich phases (Vernon, 1923). This highlighted the differential corrosion and galvanic effects within the alloy. Vernon (1927) contrasted the uniform corrosion of pure copper with the localised corrosion of brass, attributed to the latter's greater sensitivity to moisture and contaminants, due to zinc's anodic nature. Investigating indoor environments, Vernon (1931) identified the critical role of temperature and humidity fluctuations, particularly for brass. Exposure to combustion products

(containing SO_2, CO_2, and HCl) combined with these fluctuations accelerated dezincification, the selective leaching of zinc, leaving a weakened copper-rich structure. He demonstrated that high humidity, high temperatures, and these gases synergistically accelerated copper corrosion.

In the 1950s and 1960s, amid a critical increase in atmospheric pollution, concerns over the degradation of artistic heritage drove studies that continued into the 1990s, when the implementation of environmental policies gradually began to mitigate these effects (Bernardi, Chiavari, et al., 2009; European Environment Information and Observation Network - Eionet, 2020; Knotkova & Kreislova, 2007).

Since the 1980s, the United Nations (UN) has published various reports on the effects of acidic agents on structures, some of which are specifically aimed at the preservation of historical monuments. This growing interest led to the creation of the *International Cooperative Programme on Effects of Air Pollution on Materials, including Historic and Cultural Monuments* (UN ECE-ICP Materials), which aims to assess and monitor the impacts of atmospheric pollution on heritage materials. As a result of this international programme, various cooperative initiatives have been developed at the local level, such as the *International Co-operative Programme on Effects on Materials including Historic and Cultural Monuments* (ICP Materials), which focuses on studying and monitoring corrosion and soiling in cultural heritage across different environmental settings.

The advancement of heritage conservation research brought forth new analytical techniques for detailed study of patina and corrosion on metals and alloys, including copper alloy sculptures. X-ray diffraction (XRD) became a fundamental tool for identifying corrosion products from the mid-20th century onwards (C. S. Smith & Barrett, 1947). Although early XRD instruments had limitations in resolution and sensitivity, potentially hindering the detection of minor corrosion products and the analysis of complex mixtures, pioneering studies demonstrated its usefulness across a range of heritage materials, including mural paintings, canvas and wood paintings, and stone (Evison, 1951; Gettens & Stout, 1958; Rawlins & Werner, 1952; W. J. Young, 1960). XRD provided crucial information on the

crystallographic composition and structure of compounds forming on metal surfaces, enabling a deeper understanding of deterioration processes.

During this period, the application of XRD in the study of copper alloys focused on the characterisation of corrosion products, enabling a better understanding of the deterioration processes and their evolution under different environmental conditions. Research by Farnsworth et al. (1949), Gramme and Weill (1952), Weill (1952), Gettens (1949, 1961), Werner (1969), among others, was fundamental in identifying the most common corrosion compounds in these alloys using this analytical technique.

Another notable example is the study conducted by Oddy and Hughes (1970) at the British Museum, where XRD was applied to monitor the effects of stabilisation treatment on actively corroded bronzes through immersion in sodium sesquicarbonate baths. This research enabled the evaluation of the treatment's effectiveness in mitigating harmful corrosion products, thereby informing the development of long-term conservation strategies within heritage collections. A broader examination of the evolution of conservation methodologies for metal objects will be presented in Chapter 8.

The use of scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDS) has represented a significant advancement in the characterisation of the composition and microstructure of copper alloys and in the study of corrosion processes. Since the 1980s, this technique has become firmly established both in industry and in the field of cultural heritage, enabling high-resolution imaging and precise elemental analysis of metallic surfaces. SEM-EDS provides information about the morphology and elemental composition of the patina, allowing researchers to identify different corrosion layers and their spatial distribution. This is a significant advantage over bulk analysis techniques like XRD.

An example of its application in the heritage field can be found in studies conducted on metals present in historical textiles from the Metropolitan Museum of New York, which have helped identify and understand the deterioration mechanisms affecting these materials (Indictor et al., 1988; Indictor & Blair, 1990; Indictor & Koestler, 1986; Montegut et al., 1992). Additionally, since the early 2000s, there has been a growing use of SEM-EDS in the

analysis of corrosion samples from archaeological heritage objects, allowing for a detailed characterisation of the various types of corrosion present in copper alloys. This advancement has been crucial in developing conservation and restoration strategies based on precise knowledge of the composition and distribution of corrosion products (Casaletto et al., 2010; Chiavari et al., 2010; Filippo et al., 2010; Masi et al., 2017; Matthiesen et al., 2003; Neff et al., 2005; Nord et al., 2001, 2005; Rezić et al., 2010).

SEM-EDS, while offering significant advantages in characterising material composition and microstructure, is fundamentally an invasive technique requiring sample extraction. This inherent limitation restricts its applicability to sculptures and large-format objects, where sample removal is feasible and ethically acceptable. Furthermore, the representativeness of the analysis is a key concern; the small sample size typical of SEM-EDS may not accurately reflect the compositional heterogeneity of patina across a large surface. Consequently, multiple samples from diverse locations are often necessary for a comprehensive understanding of corrosion processes. However, when small sample extraction *is* permissible, SEM-EDS remains a crucial technique, providing detailed information on composition and conservation status that contributes significantly to cultural heritage preservation.

4.3 STATE OF THE ART IN THE ANALYTICAL STUDY OF COPPER ALLOY SCULPTURES: METAL COMPOSITION AND CORROSION

Note on terminology

*In the field of sculpture, the term **bronze** is commonly used to refer to copper alloys employed in artistic production, regardless of their precise composition. However, since Chapters 4.2 to 6 focus on the scientific analysis of these sculptures, the term **copper alloy** will be used instead. This choice ensures technical accuracy by avoiding generalisations and precisely reflecting the chemical composition of each analysed sculpture.*

4.3.1. The Role of Analytical Techniques in the Conservation of Copper Alloy Sculptures

The conservation of copper alloy sculptures requires a deep understanding of their materials, manufacturing processes, and deterioration mechanisms. In this context, analytical techniques are essential tools for comprehending the complexity of these objects and making informed conservation decisions.

This state of the art explores the fundamental role of analytical techniques in the conservation of copper alloy sculptures. Based on a review of the scientific literature, it provides an overview of the most relevant techniques for their study, analysing their principles, applications, and limitations within the field of conservation. It also examines their use in different contexts, from in situ analysis of monumental sculptures to detailed laboratory studies. Additionally, it identifies current trends and key challenges in this field, such as the need to improve access to these techniques and the training of specialists. Finally, it highlights the importance of analytical studies in conservation decision-making, covering

material identification, manufacturing processes, treatment evaluation, and the development of preventive conservation strategies.

As outlined in the previous subchapter, the scientific analysis of copper alloy sculptures and their corrosion processes has evolved significantly since the 18th century, progressing in parallel with technological advancements. This evolution has led to a deeper understanding of the relationship between alloy composition and long-term material transformations, such as the formation of patinas and other corrosion phenomena. Only through rigorous scientific investigation can the conservation state of these sculptures be accurately assessed, providing essential data for the implementation of restoration, conservation, and preventive intervention strategies.

Although copper alloys are often perceived as inherently resistant to environmental factors and pollution, their stability largely depends on external conditions and previous treatments. A detailed analytical approach not only enables the precise identification of metal alloy compositions and degradation mechanisms but also facilitates the development of targeted conservation strategies that ensure both the structural integrity and historical value of these sculptures.

According to Nasrazadani and Hassani (2016), advancements in analytical techniques in this field have been primarily driven by industrial applications, where the economic relevance of copper alloys has encouraged innovation. Industrial studies have accurately characterised the mechanical and chemical properties of these materials, optimising their corrosion resistance under various conditions (Chang et al., 2020; Vora et al., 2013; E. Zhang et al., 2016).

In the artistic and heritage conservation fields, analytical techniques have significantly contributed to the study of composition and deterioration processes in sculptures. Research has been conducted both through the direct analysis of original artworks and laboratory-based experimental simulations (Otmačić Ćurković et al., 2012), leading to a deeper understanding of deterioration mechanisms and the development of more effective protection strategies.

In the cultural heritage sector, analytical techniques have been primarily applied to archaeological copper alloys, particularly in countries with extensive historical legacies, such as Portugal. Studies on excavated artefacts have incorporated non-invasive methods such as EDXRF, along with minimal-sampling techniques that allow for analyses using XRD or SEM-EDS. These approaches have been extensively documented (Beltrame et al., 2018; Bottaini, Brunetti, Bordalo, et al., 2018; Bottaini, Brunetti, Montero-Ruiz, et al., 2018; Bottaini et al., 2015, 2019; Bottaini & Vilaça, 2022; E. Figueiredo et al., 2016), demonstrating their effectiveness in the characterisation of historical metal objects.

The study of large-scale archaeological sculptures has particularly benefited from these analytical advancements, especially for objects recovered from marine environments or excavation sites, where structural deterioration is often severe. The fragmentation and embrittlement of these objects facilitate sample collection without compromising their integrity, allowing for detailed assessments of their composition and corrosion processes.

While research on archaeological metal sculptures is well-established, the systematic study of modern copper alloy sculptures remained relatively unexplored until approximately a decade ago (M. L. Young & Dunand, 2015). However, recent years have seen a significant increase in research efforts, particularly in Europe and North America, leading to the development of key references in this field. In Portugal, however, studies on modern copper alloy sculptures remain scarce, a gap that will be examined further in this chapter.

Recent investigations have provided valuable insights into the composition of contemporary copper alloys and contributed to a better understanding of modern artistic casting technologies. Additionally, these studies have been crucial in differentiating between intentionally applied patinas and corrosion products formed through environmental exposure. Such distinctions are fundamental in the development of effective conservation and restoration strategies for these artworks.

4.3.2 Analysis of copper alloy sculptures: techniques and approaches

The characterisation of copper alloy compositions is fundamental for understanding manufacturing processes, mechanical properties, and long-term stability of sculptures. The choice of analytical techniques depends on factors such as the level of precision required, the invasiveness of the method, and the conservation context.

XRF and SEM-EDS stand out as the most widely employed methods, particularly due to their ability to provide non-invasive and non-destructive information in the case of XRF, and high-resolution elemental analysis in the case of SEM-EDS. Other techniques, such as ICP-based methods, X-Ray Photoelectron Spectroscopy (XPS), Atomic Absorption Spectrscopy (AA) and Particle-Induced X-ray Emission (PIXE), are utilised for more detailed laboratory analyses that require sample extraction. Figure 4.1 below illustrates the distribution of analytical techniques used in the study of copper alloy compositions, based on a review of the relevant literature concerning the analytical study of sculptures on a global scale.

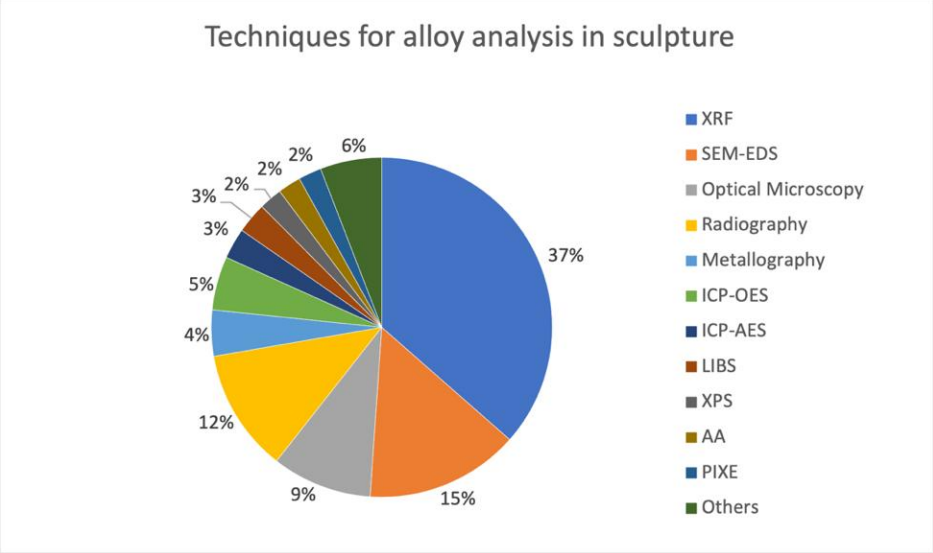


Fig. 4.1 - Distribution of analytical techniques used for alloy composition studies in copper alloy sculptures. *Others* include XES, Alpha-Spectrometry, Tomography, Lead Isotope Analysis, and ICP-MS.

Among the most commonly used tools for determining alloy composition, XRF spectrometry stands out, with its portable version gaining particular importance due to its portability and ease of use. The in situ application allows for the study of sculptures without the need for sample extraction, making it especially useful for monumental pieces or those located in hard-to-reach areas (F. G. Bewer & Scott, 1995; G. Buccolieri et al., 2015; Ferretti et al., 1997).

This technique is particularly valuable for monumental sculptures and museum collections, where transportation and intervention are restricted. Portable energy-dispersive XRF (pEDXRF) enables rapid compositional analysis of multiple areas within the same artwork, facilitating comparative studies and optimising conservation decision-making (Caridi, Paladini, et al., 2023; Carò & Megens, 2020; Ganio et al., 2014; General-Toro et al., 2021; Pouyet et al., 2019; Šatović et al., 2013). Additionally, the possibility of conducting comparative studies on copper alloy sculptures without compromising the integrity of the artworks has reinforced EDXRF's role in material diagnostics and the identification of surface alterations.

However, XRF has certain limitations, particularly when dealing with corrosion layers or heterogeneous surfaces, which can affect the accuracy of elemental readings. In such cases, Laser-Induced Breakdown Spectroscopy (LIBS) provides a complementary solution, as it enables the analysis of internal metal layers by ablating small amounts of material (Foresta et al., 2012; Siano & Agresti, 2015). Although considered a low-impact technique, its destructive nature requires careful assessment from a conservation standpoint to prevent potential damage to the artwork.

Consequently, XRF and LIBS are frequently used in combination, with the former applied to areas with minimal corrosion and the latter employed in regions where deeper compositional analysis is required (Arafat et al., 2013; Ferretti et al., 2007). This complementary approach ensures a more accurate diagnosis of alloy composition, balancing the need for precision and conservation ethics.

Similarly, laboratory methods, which are inherently invasive, provide more detailed insights into the composition of copper alloys. Among these, Inductively Coupled Plasma Mass Spectrometry (ICP-MS) is particularly effective in detecting trace elements, offering key data on alloying components and potential material sources (Snyder et al., 2017). Likewise, Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) enables precise quantification of metallic components, facilitating in-depth studies on casting alloys and their evolution over time (Gullman & Törnblom, 1994; M. L. Young et al., 2009). Although less frequently applied, Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) also provides valuable elemental analysis in heritage metal studies (Castelle et al., 2020; Karniš Vidovič & Mille, 2017; Mille & Descamps-Lequime, 2017).

SEM-EDS plays a fundamental role in microstructural analysis and elemental mapping, allowing researchers to identify manufacturing defects, grain structures, and secondary phases that influence both the mechanical properties and corrosion behaviour of sculptures (Chiavari et al., 2007; Cicileo et al., 2004; R. Fontinha & Salta, 2018; Kwon, 2023; Masi et al., 2020; Randall, 2016).

Another widely used technique in heritage analysis is PIXE, which enables elemental composition assessment with high sensitivity. Applied to metal alloys, it has proven useful in identifying alloying elements (Gyódi et al., 1999; Karniš Vidovič & Mille, 2017; Mille & Descamps-Lequime, 2017; Šatović et al., 2013).

The evolution of analytical techniques has deepened the understanding of copper alloys in sculpture, revealing variations in composition linked to historical casting methods and the impact of environmental exposure. However, characterising the metal alone is insufficient for conservation purposes, the interaction between alloy composition and corrosion processes must also be examined, as this relationship directly influences material degradation and preservation strategies.

4.3.3 Analysis of Corrosion in Copper Alloys sculpture: Techniques and Approaches

Understanding the corrosion mechanisms affecting copper alloy sculptures is essential for assessing material degradation, evaluating previous conservation treatments, and formulating preventive conservation strategies. While copper alloys are often considered resistant to environmental factors, their stability depends on a combination of external conditions, intrinsic material properties, and past interventions.

To achieve this, a variety of analytical techniques are employed, each offering specific advantages depending on the research objectives. Among these, XRD and SEM-EDS are the most frequently used methods, providing essential data on crystalline corrosion products and surface morphology, respectively. Spectroscopic and electrochemical techniques, such as Raman, FTIR, and Electrochemical Impedance Spectroscopy (EIS), complement these methods by offering insights into the composition and stability of corrosion layers. The Figure 4.2 illustrates the distribution of analytical techniques used in the study of corrosion in copper alloy sculptures, based on a review of the relevant literature.

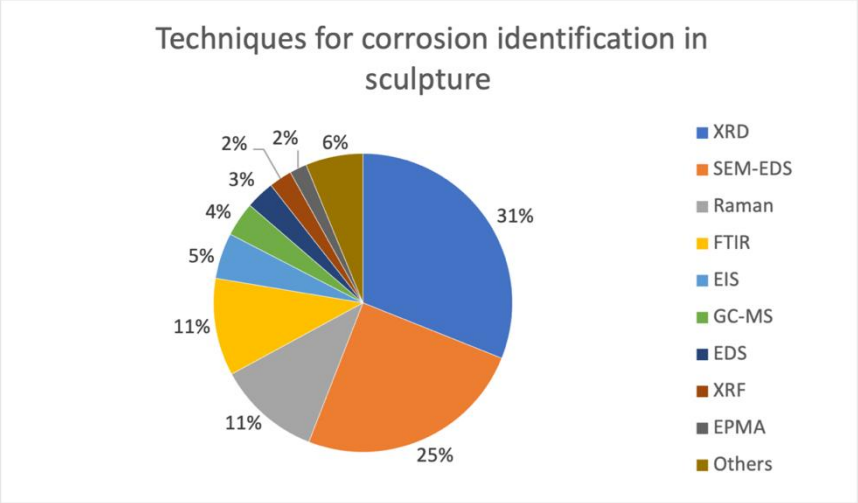


Fig. 4.2 - Distribution of analytical techniques used for corrosion studies in copper alloy sculptures. *Others*, including PIXE, IC, TEM, FIB, D-SIMS, OCP, and PLM, are applied in more specific research contexts.

In this context, XRD has emerged as one of the most widely used techniques, owing to its ability to identify crystalline corrosion products with high precision (Alunno-Rossetti & Marabelli, 1976; Floyd Brown et al., 1977; Frigerio Vidal & Iglesias Campos, 2013; Matyi & Baboian, 1986; Polikreti et al., 2009; Riederer, 1972; L. S. Selwyn et al., 1996). Unlike XRF, which provides only compositional data, XRD enables the classification of corrosion phases, offering crucial insights into the degradation pathways of copper-based sculptures (Crippa et al., 2019; Fridevaux et al., 2008; Kwon & Cho, 2023, 2024).

Similarly, SEM-EDS plays a critical role in corrosion analysis, allowing for high-resolution imaging and elemental characterisation of corrosion layers. This technique provides essential information on morphology, stratigraphy, and elemental distribution, facilitating the differentiation between protective patinas and non-protective corrosion deposits (Bogolitsyna et al., 2009; Cantini et al., 2020; Casaletto & Basilissi, 2017; Chelaru et al., 2014; Gallese et al., 2008; Pinheiro et al., 2025).

Spectroscopic techniques such as Raman and Fourier Transform Infrared Spectroscopy (FTIR) have also gained prominence, as they allow for the identification of both crystalline and amorphous corrosion products, as well as organic compounds associated with conservation treatments or environmental exposure. These methods have proven particularly useful in distinguishing between protective and destructive patinas, contributing to conservation decision-making (Langlois et al., 2017; Martín-Del-Río et al., 2018).

Recent technological advancements have facilitated the development of portable spectroscopic techniques, such as handheld Raman and FTIR spectroscopy, allowing for in situ analysis of corrosion layers (Colomban, 2012; Pozzi et al., 2021). These techniques significantly reduce the need for sample extraction while allowing sculptures to be examined within their original location indoor and outdoor. However, their analytical performance may be constrained by factors such as surface roughness and interference from complex patinas. Consequently, when a more comprehensive diagnosis is required, these methods often necessitate complementary laboratory-based analysis to ensure greater accuracy and depth of interpretation (Bracci et al., 2016; Cantisani et al., 2024).

EIS offers a unique advantage in assessing the protective properties of corrosion layers. (Casaletto & Basilissi, 2017; Es Sebar et al., 2021; Letardi & Luciano, 2007; Otmačić et al., 2021). EIS provides real-time data on corrosion kinetics, making it particularly useful for evaluating the long-term effectiveness of conservation coatings. However, its application in heritage studies remains relatively limited due to the complexity of data interpretation and the need for controlled testing conditions (Ramírez Barat et al., 2015).

Gas chromatography-mass spectrometry (GC-MS) has also been employed to analyse organic compounds associated with corrosion, such as residues from past treatments or environmental contaminants. Studies on Renaissance and Baroque copper alloy sculptures have demonstrated that GC-MS is highly effective in identifying historical coatings (Basso et al., 2020; Bongiorno et al., 2016; Masi et al., 2019; Pitthard et al., 2011; Stone, 2010; Stone et al., 1990), contributing to a better understanding of past conservation practices. However, its use is generally complementary to inorganic analytical methods, as it focuses on organic materials rather than the corrosion process itself.

The choice of analytical techniques for corrosion studies is highly dependent on the research objective. For general diagnosis of alloy composition or corrosion, XRF, XRD and SEM-EDS provide a solid foundation. If a deeper understanding of environmental impact on degradation is required, electrochemical and chromatographic techniques offer valuable complementary insights. Given the complexity of corrosion mechanisms, a multi-technique approach remains essential to obtain a comprehensive assessment of conservation challenges.

4.3.4 Multi-technique Approaches in the Characterisation and Conservation of Copper Alloy Sculptures

One of the most significant findings in conservation science is that the characterisation of copper alloy sculptures cannot rely on a single analytical technique. Instead, researchers must combine complementary methods to achieve a comprehensive diagnosis.

In studies focusing on alloy composition, XRF and SEM-EDS are frequently used together to determine elemental distribution and microstructural characteristics, providing essential data on casting techniques and material properties (Baglioni et al., 2009; R. Fontinha & Salta, 1996a, 1996b, 1996c; General-Toro et al., 2021; Masi et al., 2020; Randall, 2016; Salta & Fontinha, 1998a, 1998b, 1998c; Serafim, 2011). However, when more precise elemental quantification is required, ICP-based techniques provide greater accuracy in trace element detection. (Salvioli et al., 2017; M. L. Young et al., 2009; M. L. Young & Dunand, 2015).

In certain cases, for artefacts of suitable size, radiographic techniques can be employed to examine internal structures, detecting manufacturing features, defects, or previous restorations that are not visible on the surface (Basset, 2008; F. G. Bewer & Scott, 1995; Díaz Martinez, 2015; Mattusch, 1997; Michalopoulou et al., 2017; Siano et al., 2017; Siano & Agresti, 2015).

For corrosion analysis, a combination of XRD, SEM-EDS are the most commonly employed techniques, as they enable the identification of crystalline corrosion products and surface morphology, respectively (Basso et al., 2020; Bogolitsyna et al., 2009; Cantini et al., 2020; Chelaru et al., 2014; Chiavari et al., 2006; Frank-Kamenetskaya et al., 2019; Neiva et al., 2008; Nica-Badea & Pasāre, 2012; Pollini & Giumlia-Mair, 2019). Spectroscopic methods, including Raman and FTIR, complement these techniques by identifying amorphous phases and organic compounds associated with corrosion layers (G. Buccolieri et al., 2020; Chiavari et al., 2013; Couture-Rigert et al., 2012; Masi et al., 2017; Piccardo et al., 2013; Robbiola, Fiaud, & Pennec, 1993; Ropret & Kosec, 2012; Villegas Sánchez et al., 2009).

Electrochemical techniques, such as EIS, further contribute by assessing the stability and protective properties of corrosion layers, allowing for a better understanding of the effectiveness of conservation treatments (Es Sebar et al., 2021; Letardi & Luciano, 2007; Mikić et al., 2021; Otmačić et al., 2021).

The integration of multiple methodologies not only enhances diagnostic accuracy but also provides a more holistic understanding of how alloy composition, environmental exposure, and previous treatments interact over time. As analytical technologies continue to evolve, adopting a multi-technique approach will be essential for refining risk assessment models, optimising conservation strategies, and ensuring the long-term preservation of copper alloy sculptures.

4.3.5 Global Perspectives on Copper Alloy Sculpture Research: Methodologies, Corrosion Studies, and Conservation Practices

The study of copper alloy sculptures has followed distinct research trajectories across different countries, shaped by historical traditions, conservation priorities, and access to scientific infrastructure. While scientific research on metallic heritage has expanded significantly in the last decades, the distribution of studies remains uneven, with certain countries leading in both methodological advancements and volume of publications.

Among European nations, Italy stands out as the principal centre for research on copper alloy sculptures, particularly in the fields of archaeological, historical and modern bronzes. The country has developed extensive scientific collaborations between museums, universities, and conservation institutions, with a strong emphasis on the characterisation of metal alloys. By far, XRF is the most widely used technique for alloy analysis (A. Buccolieri et al., 2016; G. Buccolieri et al., 2015; Caridi, Mancini, et al., 2023, 2023; Caridi, Paladini, et al., 2023; Cesareo et al., 2006; Es Sebar, Iannucci, Parvis, et al., 2022; Ferretti et al., 1997; Gallese et

al., 2008), while SEM-EDS, LIBS, ICP-OES, and Atomic absortion Spectroscopy (AA) are also applied to a lesser extent (Bassini, 2011; Cantini et al., 2020; Casaletto & Basilissi, 2017; Ferretti et al., 2007; Foresta et al., 2012; Pollini & Giumlia-Mair, 2019; Siano et al., 2017). In studies focusing on corrosion processes, the most commonly employed methods in the reviewed literature include SEM-EDS, XRD, Raman, and FTIR (Alunno-Rossetti & Marabelli, 1976; Bongiorno et al., 2016; Cantisani et al., 2024; Casanova Municchia et al., 2016; Catelli et al., 2018; Crippa et al., 2019; Es Sebar et al., 2021; Es Sebar, Iannucci, Grassini, et al., 2022; Es Sebar, Iannucci, Parvis, et al., 2022).

Italian research has significantly advanced the understanding of bronze casting technologies from antiquity to modern sculpture, reinforcing the country's leadership in the technical study of sculptural heritage.

Research in France and Spain, although not as extensive as in Italy, has also played a significant role in advancing the understanding of copper alloy sculptures. Studies in these countries have focused on both archaeological and historical artworks, with notable contributions in the analysis of urban and museum-held bronzes.

In Spain, studies on bronze sculptures have primarily focused on the characterisation of alloys, frequently using non-invasive techniques such as XRF to determine elemental composition. The reviewed literature indicates that XRF is by far the most commonly employed method for this purpose, followed by techniques such as SEM-EDS, ICP-OES and, when feasible, radiography (Amigó Borrás & Cebrián Alonso, 2005; Arias Riera, 2015; Díaz Martinez, 2015; Donate et al., 2015; Nogales Basarrate et al., 2023; Villegas Sánchez et al., 2009). In parallel, some studies have incorporated corrosion analysis, aiming to understand the influence of environmental factors on surface degradation. In this context, XRD and SEM-EDS are the most frequently applied techniques for characterising corrosion products, while EIS is employed to evaluate corrosion resistance (García Peiró et al., 2015; Martín-Del-Río et al., 2018; Ramírez Barat et al., 2015; Villegas Sánchez et al., 2009).

In France, research has focused on the preservation of both indoor and outdoor 19th- and 20th-century copper alloy sculptures. French studies have significantly contributed to the

diagnosis of corrosion phenomena and the development of conservation treatments, often employing laboratory-based techniques that differ from those commonly used in Italy and Spain, particularly in early studies dating back to the 1990s.

According to the reviewed literature, the most frequently used techniques for alloy analysis in France have been Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) and XRF, with radiography applied when feasible. Additionally, Particle Induced X-Ray Emission (PIXE), tomography, and Flame Atomic Absorption Spectrometry (FAAS) have also been employed (Castelle et al., 2020; Mechling et al., 2018; Mille & Descamps-Lequime, 2017; Pouyet et al., 2019; Robbiola et al., 2008). In corrosion studies, SEM-EDS, XRD, and Raman spectroscopy have been used. Furthermore, the corrosion of certain sculptures has been examined using Transmission electron microscopy (TEM), Electron probe microanalysis (EPMA), PIXE, FTIR, and GC-MS (Chiavari et al., 2007; Robbiola, Fiaud, & Pennec, 1993; Robbiola et al., 2008; Robbiola & Hurtel, 1991).

In other European countries, the reviewed literature indicates that research has predominantly concentrated on the analysis of corrosion processes in bronze sculptures. Techniques such as XRD, SEM-EDS, FTIR, Raman spectroscopy, and ion chromatography (IC) are among the most frequently employed methods for identifying corrosion products (Bogolitsyna et al., 2009; Chelaru et al., 2014, 2022; Frank-Kamenetskaya et al., 2019; Nica-Badea & Pasāre, 2012; Otmačić et al., 2021; Polikreti et al., 2009; Ropret & Kosec, 2012; Strandberg, 1997). In terms of alloy characterisation, XRF is the most widely used technique, followed by ICP-based methods (Karniš Vidovič & Mille, 2017; Lehmann et al., 2010; Michalopoulou et al., 2017; Riederer, 1972). Where circumstances have permitted, optical microscopy and radiography have also been applied to study the internal structure and manufacturing features of the metal (Frank-Kamenetskaya et al., 2019; Karniš Vidovič & Mille, 2017; Michalopoulou et al., 2017; Mikić et al., 2021).

The long-term exposure of monumental copper alloy sculptures to airborne contaminants and industrial emissions has been a primary concern in European conservation science,

leading to extensive studies on the effectiveness of protective coatings and preventive conservation strategies.

In the United States, research on copper alloy sculptures has been primarily conducted by conservation departments within museums, universities, and independent research centres. Unlike in Europe, where historical metallurgical studies have played a central role, U.S. research has been more oriented toward applied conservation and preventive strategies. Moreover, investigations have focused predominantly on sculptures produced in the 19th and 20th centuries, primarily of European origin, alongside studies on ancient European and Asian copper alloy artworks.

For alloy characterisation, the most commonly used techniques include XRF and radiographic analysis, particularly for sculptures housed in museums (Basset, 2008; F. G. Bewer & Scott, 1995; Borsch et al., 2018; Day et al., 2010; Lefferts et al., 1981; Maish, 2017; Mattusch, 1997; Randall, 2016). Other techniques referenced in the literature include SEM-EDS, metallography, and ICP-based methods (Chiavari et al., 2007; Floyd Brown et al., 1977; Hemingway & Hemingway, 2003; Salvioli et al., 2017; Snyder et al., 2017; M. L. Young et al., 2009; M. L. Young & Dunand, 2015). Research in the U.S. has largely prioritised alloy composition over the historical reconstruction of casting techniques, reflecting a conservation-driven rather than an archaeological or art-historical approach.

In corrosion studies, the most frequently applied techniques are XRD, GC-MS, SEM-EDS, and FTIR (Day et al., 2010; Lefferts et al., 1981; Mattusch, 1997; Matyi & Baboian, 1986; Meakin et al., 1992). GC-MS has been specifically employed in the analysis of Renaissance copper alloy sculptures to characterise organic compounds associated with past treatments or environmental interactions (Basso et al., 2020; Stone, 2010; Stone et al., 1990).

Beyond geographically oriented studies on existing copper alloy sculptures, a significant body of research has emerged in laboratory settings focused on the behaviour of metal alloys under controlled conditions. While a considerable proportion of these studies has been directed towards archaeological bronzes, an increasing number of investigations explore corrosion phenomena in non-archaeological contexts. These include systematic analyses of

corrosion rates and mechanisms under diverse atmospheric conditions, aiming to simulate long-term exposure scenarios (Bernardi, Chiavari, et al., 2009; Chiavari et al., 2006, 2010, 2011, 2022; Masi et al., 2017; Svara Fabjan et al., 2011).

In this regard, artificial patinas have been developed to replicate aged surfaces and to better understand the stratigraphy and stability of corrosion layers (Chiavari et al., 2009; R. González-Parra et al., 2023; Kapitanovic & Otmačić Ćurković, 2022; Z. Wang et al., 2023). Analytical methods have also been employed to monitor the development of corrosion on the alloy surface over time and under varying environmental conditions (Kosec et al., 2024; Krätschmer et al., 2002; B. Li et al., 2025; Oliveira et al., 2009; Papadopoulou & Vassiliou, 2021; Porcu et al., 2022). Furthermore, some studies have incorporated variables associated with non-environmental factors, such as exposure to organic acids, for example, uric acid from bird droppings, which can significantly accelerate degradation processes in sculptures located in public spaces (Arroyo Ginez et al., 2018; Balogh et al., 2017, 2019; Bernardi, Bowden, et al., 2009).

In parallel, laboratory-based research has increasingly examined the efficacy of both historical and contemporary protective coatings. These studies have included the evaluation of materials traditionally used in conservation, such as lacquers and natural resins (Galeotti, M. et al., 2024; Pitthard et al., 2011), as well as synthetic and biological coatings designed to enhance long-term surface stability (Abbas et al., 2021; Albini et al., 2016, 2017; Chiavari et al., 2013, 2015; X. Li et al., 2024; Novak & Kosec, 2022). In addition, certain studies have focused on assessing the performance of individual analytical methods specifically in the identification of corrosion products. (Balta et al., 2009; Di Francia et al., 2021; Grayburn et al., 2015; Mazzeo & Joseph, 2007; Ropret & Kosec, 2012; Šatović et al., 2013).

Although not always linked to specific sculptural case studies, these laboratory investigations provide fundamental insights into corrosion dynamics and the performance of conservation materials, offering broad potential for application in the preservation of metallic heritage.

4.3.5.1 Scientific research on copper alloy sculptures: Portuguese context

The study of copper alloy sculptures in Portugal has followed a different trajectory. Although fewer analytical studies have been conducted compared to Italy or France, the application of scientific techniques in Portuguese research has provided valuable insights into the composition and conservation of public monuments. A key milestone in this field was the work carried out by the National Laboratory of Civil Engineering (LNEC) in the 1990s, particularly through the research of Isabel Rute Fontinha and M. Manuela Salta. Their studies focused on the characterisation of alloys, corrosion processes, and conservation strategies for monumental sculptures in Lisbon and Porto, leading to a series of investigations that established a scientific foundation for the study of these materials in Portugal.

Between 1995 and 1998, emblematic sculptures such as the Monument to the *Marquês de Pombal*, the Monument to the *Duque de Saldanha*, and the Monument to *King José I in Lisbon* , as well as the statues of *King Pedro IV*, *King João VI*, and *Júlio Dinis* in Porto (R. Fontinha & Salta, 1996b, 1996a, 1996c), were analysed. These investigations formed part of the national project *"Tecnologias de conservação de monumentos em ligas de cobre"*, under the EUREKA EU316 EUROCARE COPAL programme.

These studies incorporated methodologies for the characterisation of alloy and corrosion products, applying techniques such as EDXRF, SEM-EDS, and metallographic analysis to assess the degradation layers in detail. Additionally, polarised light microscopy and XRD were used to identify specific corrosion compounds, contributing to a better understanding of deterioration processes in urban settings.

The experience gained from these analytical studies led to the publication of *Metodologia para o diagnóstico da corrosão em estátuas de ligas de cobre* by LNEC in 2000 (I. R. Fontinha & Salta, 2000), a reference document for the application of scientific methods in corrosion diagnostics. Likewise, the analyses conducted on the statue of *King José I* played a fundamental role in planning its restoration in 2012 and 2013, with the findings compiled

in a report detailing the methodologies and conservation strategies employed (R. Fontinha & Salta, 2018).

4.3.5.2 Analytical techniques and key findings

The methodologies used in Portugal closely align with those employed in Italy, France, and other European countries, with studies applying SEM-EDS, EDXRF, Raman spectroscopy, and XRD for the characterisation of both alloys and corrosion products. However, an important distinction lies in the focus of the studies: while Italy has prioritised the study of archaeological and historical copper alloy sculptures, Portuguese research has predominantly concentrated on outdoor public sculptures and conservation projects.

A significant example of the application of analytical techniques in Portugal is the 2011 study of *Jean d'Aire* by Auguste Rodin, belonging to the *Fundação Calouste Gulbenkian* (Serafim, 2011). This research involved the use of EDXRF, XRD, FTIR, Raman spectroscopy, SEM-EDS, metallography, and optical microscopy to assess the sculpture's alloy composition and surface corrosion products. The results revealed the presence of copper sulphates, chlorides, and nitrates, the latter associated with exposure to fertilisers in the garden where the sculpture is displayed. Additionally, cyanide compounds were identified, derived from the artificial patina applied to the artwork.

The 2021 study on the statue of *King Afonso Henriques* in Guimarães applied EDXRF, powder x-ray diffraction (pXRD), SEM-EDS, optical microscopy and metallography to characterise both the metal alloy and the patina (General-Toro et al., 2021). The study, conducted by the HERCULES Laboratory at the Universidade de Évora, focused on identifying variations in alloy composition, the impact of environmental exposure, and the structural integrity of the sculpture's surface layers. The results provided valuable data on the conservation state of the artwork, highlighting areas affected by corrosion and

degradation mechanisms linked to long-term exposure to outdoor conditions. The methodology used, along with the results obtained, is presented in Chapter 5 of this study.

More recently, in 2023, the HERCULES Laboratory conducted an analytical study on the statue of *Eusébio da Silva Ferreira* (cast in 1992), located in front of Benfica's football stadium in Lisbon (Pinheiro et al., 2025). The analysis focused on both the alloy composition and corrosion phenomena, employing EDXRF, μXRD and SEM-EDS. The study revealed that the statue is composed of a ternary copper-tin-zinc alloy with a high lead content. Regarding corrosion processes, dezincification was identified in certain areas, manifested as whitish zinc salts, while tin oxides were detected in other regions. Additionally, gypsum and calcite formations were found, likely resulting from atmospheric pollution.

The scientific study of copper alloy sculptures in Portugal has primarily focused on public monuments and conservation diagnostics, aligning methodologically with broader European research. Early studies by the LNEC established a foundation for corrosion assessment and conservation treatments, which has been expanded by recent investigations from institutions like the HERCULES Laboratory. The continued application of advanced analytical techniques ensures the preservation of Portugal's sculptural heritage, reinforcing the importance of interdisciplinary collaboration in this field.

4.4 FINAL REMARKS ON CHAPTER 4

The analytical study of copper alloy sculptures has become an essential field within conservation science, offering valuable insights into material composition, degradation mechanisms, and preservation strategies. While research has advanced significantly over the past decades, its development has been shaped by regional priorities, institutional frameworks, and access to scientific infrastructure. European countries such as Italy, France,

and Spain have led studies on historical and archaeological copper alloy sculptures, often integrating conservation science with art-historical and technological investigations. In contrast, research in the United States has been more focused on the applied conservation of 19th- and 20th-century sculptures, reflecting the nature of collections housed in major institutions. In Portugal, despite a more limited volume of studies, research efforts have made significant contributions to the understanding of outdoor public sculptures, with early initiatives led by the National Laboratory of Civil Engineering (LNEC) and more recent advancements by the HERCULES Laboratory.

Despite variations in focus and methodology, a common challenge remains: the need for interdisciplinary collaboration and the continuous development of accessible analytical tools. While high-precision laboratory techniques provide detailed insights, in situ and non-invasive methods have become increasingly relevant, particularly for large-scale and immovable artworks. The integration of multiple analytical approaches is essential for achieving a comprehensive understanding of both alloy composition and corrosion processes, ensuring the long-term preservation of copper alloy sculptures across different cultural and environmental contexts.

To address current gaps in the field, particularly in the study of modern sculptures and the long-term evaluation of conservation treatments, further research grounded in material analysis is required. In this context, the analytical investigation of selected works by António Soares dos Reis, presented in the following chapter, aims to contribute original data and methodological reflections to the study of modern copper alloy sculpture.

These case studies not only expand the scientific understanding of alloy composition and alteration patterns in Portuguese public artworks but also offer a concrete example of how integrated analytical approaches can inform conservation decisions and strengthen the link between scientific research and heritage management.

CHAPTER 5. ANALYSIS OF SOARES DOS REIS'S BRONZE SCULPTURES: METHODOLOGY AND RESULTS

5.1 INTRODUCTION

This chapter presents an analytical investigation focused on the bronze sculptures by António Soares dos Reis, with particular emphasis on the chemical characterisation of the alloys and the study of corrosion products formed on their surfaces. A combination of non-destructive and micro-destructive techniques was applied, selected according to the type of information required, the accessibility of each sculpture, and the constraints imposed by the custodial institutions. The techniques employed include X-ray fluorescence (XRF), X-ray diffraction (XRD), optical microscopy (OM), and scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDS), as summarised in Table 5.1.

Table 5.1 Analytical techniques employed in the study of the bronze sculptures by Soares dos Reis.

Nº	Sculpture	Setting	XRF	XRD	SEM-EDS	OM
1	Francisco de Almada e Mendonça	Outdoor (Porto)	X	X		
2	King Afonso Henriques	Outdoor (Guimarães)	X	X	X	X
3	S. José	Indoor (MNSR)	X	X		
4	S. Joaquim	Indoor (MNSR)	X	X		
5	João Marques de Oliveira	Outdoor (Porto)	X	X		
6	Figura Feminina	Outdoor (Porto)	X	X		
7	Busto de Firmino	Indoor (MNSR)	X			
8	O Pescador	Indoor (MNSR)	X			
9	Academia – Homem Sentado	Indoor (MNSR)	X			
10	Francisco Pinto Bessa	Indoor (MNSR)	X			
11	A Riqueza	Indoor (MNSR)	X			
12	A Música	Indoor (MNSR)	X			
13	O Trabalho	Indoor (MNSR)	X			

Access to the sculptures was determined by a range of physical, logistical and administrative factors, which influenced the feasibility of applying each analytical technique. One of the most relevant cases was the statue of King Afonso Henriques in Guimarães, where it was possible to carry out a full analytical campaign using all selected techniques, including the

rare extraction of a metallic sample, an uncommon practice in heritage sculpture studies. The results of this investigation were subsequently published by General-Toro et al. (2021).

The collection of corrosion product samples also presented significant challenges. In outdoor sculptures, where corrosion layers were more abundant due to the absence of previous conservation interventions, it was possible to extract material without compromising visual integrity. In contrast, indoor museum-held pieces, particularly those subjected to preventive conservation programmes, offered more limited opportunities for sampling. The only sculptures for which sampling was authorised were S. José and S. Joaquim, both of which had been temporarily removed from the museum's permanent exhibition at the time of intervention.

In these cases, sampling was carried out in discrete, non-visible areas with partially altered artificial patinas, following criteria of minimal intervention and respect for the aesthetic perception of the artworks. These areas were selected due to their low visibility and to ensure they did not significantly affect the visual reading of the artwork.

The selection of sculptures and techniques, as well as the organisation of the results, follows a comparative framework structured into two main categories of analysis: alloy composition and corrosion products. Priority was given to sculptures presenting data in both categories, and they are presented in chronological order according to their casting date. This methodological approach provides a basis for the comparative analysis developed in section 5.4 and supports the interpretative and conservation-focused discussions presented in the following chapters.

Although bronze alloys in sculpture are generally composed of copper, tin, zinc, and lead, the amount of lead may sometimes be so reduced (below 2%) that the alloy could be considered ternary. In the analytical studies on sculpture considered in this thesis, however, some authors have retained the designation *quaternary alloy* even when the lead content is minimal (Basset et al., 2008; Kwon, 2024; Kwon & Cho, 2024; Masi et al., 2019; Mikić et al., 2021). In this study, alloys with more than 1% lead will be classified under this category.

5.2 CHARACTERISATION METHODS AND INSTRUMENTATION APPLIED TO THE BRONZE SCULPTURES UNDER STUDY

5.2.1 Compositional Analysis Using X-Ray Fluorescence (EDXRF)

X-ray fluorescence (XRF) spectrometry has become one of the most widely employed analytical techniques in the field of Cultural Heritage, owing to its non-destructive nature, versatility, and capacity for in situ application. This methodology enables the investigation of the composition of a wide range of materials: solids, liquids, powders, or filtered solutions, yielding both qualitative and semi-quantitative results about the elemental constituents of a given sample .

The operating principle of XRF relies on the excitation of atoms within a sample by high-energy photons generated by an X-ray tube. This excitation causes the ejection of electrons from the inner shells of the atoms, and the subsequent electronic transitions generate characteristic secondary X-ray emissions specific to each element (Kalnicky & Singhvi, 2001; Stuart, 2007). Depending on the spectrometer configuration, these emissions can be detected and interpreted to determine the elemental composition, covering elements from beryllium (Be) to uranium (U) (Brouwer, 2010; Grieken & Markowitz, 2001; Potts & West, 2008; Stuart, 2007).

Quantification is achieved by counting atomic impulses whose intensity correlates with the concentration of the respective element. Meanwhile, qualitative assessment identifies the presence of specific compounds through their spectral signatures (Potts & West, 2008; Sagrera, 1966). This technique has proven especially useful in the study of copper and its alloys, both independently and in conjunction with other analytical methods (A. Buccolieri et al., 2016; Ferretti et al., 2007; General-Toro et al., 2021), and has been applied to artefacts

ranging from ancient civilisations to modern sculptures (Bottaini, Brunetti, Bordalo, et al., 2018; Bottaini et al., 2012, 2015; Gigante & Cesareo, 1998; Janssens et al., 2000).

Its applicability also extends to the analysis of metal homogeneity, the detection of modified areas, such as welds, restorations, or additions, and the inference of provenance or technical features related to casting processes. Within the framework of this project, its effectiveness has been widely recognised in the analysis of metals with natural or artificial patinas, without the need to intervene in the surface layers (Day et al., 2010; Ferretti et al., 1997; Ganio et al., 2014; Pouyet et al., 2019; Stone, 2010).

One of the main operational advantages of XRF lies in the availability of portable spectrometers, which enable direct measurement on large-format or difficult-to-handle metallic sculptures. These devices, along with models designed for macro and micro-scale analysis, have significantly broadened the applicability of this technique in heritage studies (G. Buccolieri et al., 2015; Ferretti et al., 1997; E. Figueiredo et al., 2016; Gigante & Cesareo, 1998; Kalnicky & Singhvi, 2001; Mazzeo et al., 2012).

In the present study, compositional analysis was carried out using a portable Bruker TRACER III-SD spectrometer, equipped with a rhodium anode tube and a silicon drift detector. This equipment, belonging to the HERCULES Laboratory at the Universidade de Évora, allowed for in situ data collection without the need for sample extraction, ensuring a non-destructive approach aligned with preventive conservation principles (Fig. 5.1). The analyses were conducted with two different Al/Ti filters to identify primary and secondary elements, under the following operational conditions: 10 kV and 30 μA for 100 seconds; and 40 kV and 11 μA for 100 seconds. The spectra were acquired using S1PXRF v.3.8.30 and processed with Bruker's ARTAX v.5.3.0.0 software.

To maximise consistency and reproducibility, the device was placed in direct contact with flat areas of the sculptures to ensure complete coverage of the 3×4 mm spot and to minimise atmospheric interference.



Fig. 5.1 - Example of XRF analysis. Analytical study of the sculpture *O Pescador* (The Fisherman. 1870, cast between 1922 and 1927), part of the MNSR collection. ©*Pablo General-Toro.*

It is important to note that the EDXRF analyses were conducted directly on the surface of the sculptures, without removing the superficial patina, whether natural or artificial. While this approach is methodologically conservative, it may introduce certain deviations in the results due to the presence of extraneous elements not representative of the underlying metal (Emmitt et al., 2021; Pearce, 2018; Vianello & Tykot, 2017). Nevertheless, the decision was made to preserve the integrity of the artworks, prioritising conservation criteria and adhering to the access restrictions imposed by the custodial institutions.

To mitigate the impact of the patina on elemental readings, the Monte Carlo algorithm (XRMC) was applied specifically to the statue of King Afonso Henriques. This allowed for refinement of the EDXRF results (General-Toro et al., 2021). This processing was performed at the Department of Chemistry and Pharmacy, University of Sassari, where the computational model was used to simulate the interaction of X-rays with the different material layers. This case-specific application provides a methodological example of how data can be algorithmically processed to obtain a more accurate estimate of the bronze composition without recourse to invasive or destructive techniques, even in the presence of surface interferences.

The Monte Carlo method is a statistical simulation technique that enables the virtual reproduction of X-ray interactions with layered materials (Schoonjans et al., 2011, 2012). In XRF analysis, it is particularly useful for examining metallic objects that preserve patinas or corrosion layers, as these can distort in situ surface readings (Brunetti, Golosio, Schoonjans, et al., 2015; Schoonjans et al., 2011). Through a detailed computational model, the method simulates physical processes such as absorption, emission and scattering across each layer, patina, metallic substrate and potential coatings, while accounting for variables like thickness, elemental composition, and instrumental configuration, including voltage, beam geometry, filters and detector type (Brunetti, Golosio, Schoonjans, et al., 2015; Schoonjans et al., 2011).

The XRMC software produces a synthetic spectrum that is compared to the actual spectrum. The algorithm then iteratively adjusts model parameters until statistical convergence is achieved, thereby allowing for a more accurate estimation of the underlying metal composition without direct surface intervention. This method has proven particularly appropriate for preventive conservation strategies, especially when standard quantification techniques such as the fundamental parameter method fall short due to surface irregularities or instrumental limitations (Brunetti, Golosio, Schoonjans, et al., 2015; Nocco et al., 2021). Its effectiveness has been validated through applications to both small-scale bronzes, such as Nuragic navicelle, archaeological bronze artefacts from excavation sites in Portugal, and more complex monumental objects, demonstrating its capacity to characterise stratified alloys in situ (Bottaini, Brunetti, Bordalo, et al., 2018; Bottaini et al., 2015; General-Toro et al., 2021; Nocco et al., 2021; Schiavon et al., 2016).

The results obtained from this application were published in the scientific journal *Heritage* (MDPI), as part of an article directly related to this project. A detailed discussion of these findings is included in the results section of this thesis.

5.2.2 X-ray Diffraction (XRD)

X-ray diffraction (XRD) is a widely used analytical technique for the characterisation of crystalline materials, allowing for the identification of mineral phases based on the atomic arrangement within their structure. This method is based on the interaction between monochromatic X-rays and the crystal lattice of a sample, producing specific diffraction patterns that follow Bragg's Law ($n\lambda = 2d \sin \theta$), where λ is the wavelength, θ the diffraction angle, and d the distance between crystallographic planes (Dutrow, n.d.; Stuart, 2007).

When diffraction conditions are met, the monochromatic X-rays strike the sample's crystal structure and are coherently scattered, generating a diffraction pattern that provides detailed information about the atomic arrangement of the material. The diffracted X-rays are detected, processed, and quantified by a detector, which converts the signals into a spectrum of intensity peaks. Each of these peaks corresponds to a specific crystalline phase and reflects the orientation and distribution of atomic planes within the crystal lattice (Patiño-Ruiz et al., 2020).

In the field of archaeological and historical metals, XRD has proven particularly effective for identifying corrosion products, especially those derived from copper alloys (Bogolitsyna et al., 2009; Chiavari et al., 2006; Cosano et al., 2018; Di Carlo et al., 2017; Fabrizi et al., 2019; Lutterotti et al., 2016; Megahed, 2014; Scott & Maish, 2010).

A commonly used modality for the analysis of patinas is powder X-ray diffraction, which is applied to samples of corrosion products collected from the surface of the metal(Bogolitsyna et al., 2009; Chiavari et al., 2010; Chmielová et al., 2003; Cosano et al., 2018; Di Carlo et al., 2017; Krätschmer et al., 2002). This technique was employed in the present study.

In order to characterise the corrosion products, present on the surface of the sculptures, powder samples were collected from six pieces using a scalpel (Fig. 5.2), following a minimal intervention approach. These samples were subjected to X-ray diffraction (XRD), a technique that enabled the identification of the crystalline phases present in the powder and, consequently, the understanding of the underlying corrosion mechanisms (Fig. 5.3).



Fig. 5.2



Fig. 5.3

Fig. 5.2 - Collection of corrosion powder sample from the rear area of the sculpture of *King Afonso Henriques* in Guimarães (sample DAH01-XRD). © *Pablo General-Toro.*

Fig. 5.3 - Corrosion powder sample DAH01-XRD being analysed by X-ray diffraction. © *Pablo General-Toro.*

The equipment used was a BRUKER D8 Discover μ-XRD system with DAVINCI design, equipped with a Cu Kα radiation source operating at 40 kV and 40 mA, and a LINXEYE™ one-dimensional detector. This system is part of the instrumental infrastructure of the HERCULES Laboratory at the University of Évora.

The samples, consisting of patina deposits or corrosion products extracted from the sculpture surfaces, were mounted on zero-background sample holders and irradiated using a 0.6 mm slit. The microbeam was produced via a Göbel mirror and a 1 mm collimator. Angular scanning (2θ) was performed in the 3°–70° range, with a step size of 0.02° and an acquisition time of 3 seconds per step. The interpretation of the resulting diffractograms was carried out

using the routines provided in the Diffrac.EVA software package, in combination with reference files from the PDF-2 database.

The specific areas selected for analysis were determined according to chromatic differences observed on the surface, indicative of possible variations in the composition of the corrosion products.

Traditionally, the analysis of complex mixtures using XRD presented certain limitations due to peak overlapping in the diffraction patterns, which hindered quantitative interpretation. To address this issue, Hugo Rietveld developed in 1969 a structural refinement method that enables the modelling of entire diffraction profiles, accounting for factors such as particle size, internal stress, and preferred orientation. This technique, known as Rietveld refinement, has revolutionised the quantitative analysis of crystalline phases in heterogeneous materials (Runčevski & Brown, 2021; Stuart, 2007).

XRD has been extensively used to characterise non-amorphous crystalline materials, including those present in metallic sculptures. In this context, the technique has made it possible to identify corrosion products formed through the interaction of metals with environmental contaminants such as salts and sulphates (Chmielová et al., 2003; Grayburn et al., 2015; Masi et al., 2017; Veleva & Farro, 2012; J. Wang et al., 2006; Watanabe et al., 2007; X. Zhang et al., 2014). XRD has also been used to detect organic residues, such as bird droppings, as well as conservation materials applied during previous interventions, including microcrystalline waxes frequently used for the protection of metal surfaces (Balogh et al., 2017, 2019; Rao & Zhang, 2011).

5.2.3 Optical and Electron Microscopy Techniques

Microscopy techniques play a crucial role in the conservation sciences, enabling the observation of material structures at a level of detail beyond the capabilities of the human eye. In this study, both optical and electron microscopy were employed to document surface

morphology, identify corrosion phenomena, and reveal internal microstructures of bronze sculpture.

5.2.3.1 Optical and digital microscopy

Optical microscopy (OM) is a fundamental observational technique in heritage conservation studies, enabling the analysis of constituent materials, alteration products, and stratigraphic surface layers. Its ability to examine both macroscopic and microstructural features provides insights into the presence of biodeterioration agents and the overall conservation condition of artefacts. In particular, its application to metal sculptures, especially archaeological bronzes, is essential for identifying previous interventions, corrosion products, and alterations linked to specific environmental conditions (Oudbashi & Wanhill, 2024; Qureshi et al., 2020).

OM operates on the principle of using a lens system to magnify the image of a sample illuminated by visible light. Depending on the configuration, two main modes can be distinguished: transmission microscopy, where light passes through the sample, and reflection microscopy, where light is reflected from its surface. The latter was employed in this study, as it is particularly suitable for the analysis of opaque materials such as metals and their corrosion products (Ebnesajjad, 2014).

In this context, to investigate the surface condition and internal structure of the bronze alloy, a sample was taken from the sculpture of King Afonso Henriques. This fragment, which corresponded to a casting defect, was easily detached using a scalpel during a site visit to observe cleaning works being carried out on the monumental statue by the conservation company *Oficina Santa Bárbara* in June 2021. The sample was embedded in epoxy resin and mechanically polished for microscopic observation. This preparation process, including mounting and polishing, is common to both OM and metallographic microscopy analyses. The sample was then examined using a Leica DM/LP microscope at Haute École Arc Ingénierie (Le Locle, Switzerland (Fig. 5.4).



Fig. 5.4 - Observation of the corrosion film on the fragment from the sculpture of King Afonso Henriques using polarised light microscopy at Haute École Arc Ingénierie, Le Locle, Switzerland. © *Pablo General-Toro*.

Prior to sampling, portable digital microscopy was employed in situ to document the surface condition of the sculptures and assist in the selection of areas for analysis. This technique allows for rapid, non-invasive observation of surface morphology without the need for complex handling or prior sample preparation. Its compact design, high-resolution image capture, adjustable lighting, and digital storage capabilities make it particularly valuable for the documentation of heritage objects.

In this study, two devices were used: a Dino-Lite AM7915MZT and a SkyBasic GNIMB401KH03, offering magnification ranges from 50× to 1000×. These instruments enabled detailed visual recording of corrosion phenomena, biological residues, patinas and other surface features directly on the artworks, supporting both condition assessment and future monitoring efforts.

5.2.3.2 Metallographic microscopy

Metallographic microscopy is a specialised application of reflected light optical microscopy, designed to reveal the microstructure of metals and alloys. This technique is particularly suitable for the study of opaque materials, such as heritage metal objects, as it allows the

observation of structural features that are not accessible with transmitted light methods (Carrizo, 2021; Gyöngyösi et al., 2023; Robotti et al., 2018; Scott, 1991).

The preparation of samples is crucial and follows a carefully standardised process. It involves cutting the metallic fragment, embedding it in epoxy resin, and mechanically polishing the surface until a perfectly smooth and reflective finish is obtained. This is followed by chemical etching, using reagents that reveal grain boundaries, metallic phases, and other microstructural details (Koraboyevna, 2024). The clarity and reliability of metallographic images depend directly on the precision of this preparation.

In heritage conservation, this method provides essential information for reconstructing an object's manufacturing history and diagnosing degradation. It allows the identification of grain morphology, inclusions, voids, porosities, and corrosion structures, as well as evidence of mechanical or thermal treatments associated with either the original production or later interventions (Carrizo, 2021; Scott, 1991). It also enables the detection of damage patterns, such as fissures or cracks, that may not be visible macroscopically (Lynch, 1989).

Although the technique is invasive due to the sampling required, its use is justified when detailed microstructural insight is necessary for conservation strategies. When combined with complementary methods such as XRF or SEM-EDS, it contributes to a comprehensive understanding of an object's condition and the factors affecting its long-term stability (Robotti et al., 2018; Szala et al., 2013).

In this study, the same metallic fragment from the sculpture of King Afonso Henriques, previously analysed by OM, was used for metallographic examination. After embedding and polishing, the sample was etched with a solution of $FeCl_3$ and HCl in ethanol, following the protocol described by Scott (1991).

The sample was first examined using polarised light optical microscopy at Haute École Arc Ingénierie (Le Locle, Switzerland), employing a Leica DM/LP microscope. Subsequent observations were performed at the HERCULES Laboratory, University of Évora, using a

Leica DM2500P microscope equipped with a Leica MC170HD digital camera and operated through LAS V 4.4.0 software.

5.2.3. Scanning Electron Microscopy with Energy-Dispersive Spectroscopy (SEM-EDS) and Field Emission Gun (SEM-FEG)

Scanning Electron Microscopy with Energy-Dispersive Spectroscopy (SEM-EDS) is a widely employed technique across scientific and industrial disciplines due to its applicability to both organic and inorganic materials and its capacity to deliver immediate and precise results (Ali et al., 2023; Davies et al., 2022; Girão et al., 2017). In the field of heritage science, it plays a fundamental role in the chemical identification of elements and the microstructural characterisation of materials from artworks, architectural elements, and archaeological artefacts.

Its increasing adoption has led to exponential growth in publications employing SEM-EDS, rising from approximately one thousand to over forty thousand since the 1990s, reflecting its relevance for non-destructive diagnostics and decision-making in conservation contexts (Davies et al., 2022). SEM enables high-resolution imaging at the micro- and nanoscale, significantly surpassing the capabilities of conventional optical microscopy. This allows for the visualisation of microstructural features otherwise undetectable, such as microfractures, metallic grains, inclusions, and specific corrosion phenomena (de Haan et al., 2019; X. Liu et al., 2016; Oudbashi & Wanhill, 2024).

Unlike optical microscopy, which relies on visible light, SEM employs a focused electron beam generated by an electron gun. This beam interacts with the sample surface, producing secondary electrons (SE) and backscattered electrons (BSE), which are detected to generate greyscale images with high morphological detail and quasi-three-dimensional appearance. SEM can achieve magnifications of up to one million times, but requires vacuum conditions for operation (X. Liu et al., 2016; Mohammed & Abdullah, 2019; Stuart, 2007).

EDS complements SEM by providing elemental analysis through the detection of characteristic X-rays emitted when the beam interacts with the sample's atoms. This allows both point-specific analyses and elemental mapping, proving highly effective for identifying corrosion products, inclusions, and restoration residues. EDS can also be integrated with other advanced techniques such as TEM or Scanning Transmission Electron Microscopy (STEM), expanding its application in micro- and nanoscale studies (Davies et al., 2022; Girão et al., 2017; Ismail et al., 2019).

Field Emission Gun Scanning Electron Microscopy (SEM-FEG) represents a refined SEM configuration. Unlike conventional SEMs, SEM-FEG incorporates a field emission source that produces a highly stable and focused electron beam, offering superior resolution, especially at low accelerating voltages, and enhanced surface sensitivity and contrast. This makes it particularly suitable for delicate microstructures or low-conductivity surfaces (TermoFisher Scientific, 2021).

SEM operates under vacuum conditions, unlike optical microscopy. To prevent surface charging during imaging, samples must be dry and electrically conductive. Non-conductive specimens are coated with conductive materials such as carbon or gold (Thermo Fisher Scientific Phenom-World BV, 2020). Powder samples, like corrosion products, were mounted on carbon adhesive tape, while solid fragments were sputter-coated with gold or carbon depending on the analytical goal—gold for higher image quality, carbon when elemental microanalysis was required (C. Chen, 2022; Davies et al., 2022).

To determine the elemental composition, energy dispersive X-ray spectroscopy (EDS) coupled with scanning electron microscopy (SEM) was applied. Two different instruments were used for this purpose. At the HERCULES Laboratory, University of Évora, a HITACHI S3700N SEM was employed, coupled with a Quanta EDS microanalysis system equipped with a Bruker AXS Flash silicon drift detector, offering a spectral resolution of 129 eV at FWHM/Mn Kα. Operating conditions for this analysis included secondary electron mode (SE), an accelerating voltage of 20 kV, a working distance of approximately 10 mm, and an emission current of 90 μm (Fig. 5.5).

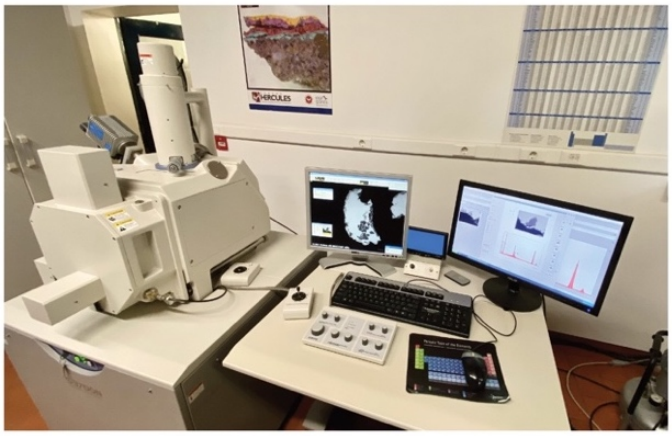


Fig. 5.5 - Observation of the same fragment using SEM-EDS at the HERCULES Laboratory, University of Évora, Portugal. © *Pablo General-Toro.*

At the Haute École Arc Ingénierie Laboratory (Le Locle, Switzerland), a SEM-FEG JEOL 7001-F was used, equipped with a silicon-drift EDS Oxford detector (Aztec analysis software). The operating voltage was 20 kV with a probe current of approximately 9 nA. The relative error is estimated at around 10% for content below 1 wt%, and 2% for content above 1 wt%.

The SEM-FEG and OM analyses, the latter of which was previously described in this chapter, were conducted during the ENDLESS Metal Short Time Scientific Mission (5–9 June 2023), organised by the European Cooperation in Science & Technology (COST) in collaboration with Haute École Arc Conservation-Restauration.

5.3 RESULTS FROM TECHNICAL ANALYSES OF SCULPTURES BY SOARES DOS REIS

This section presents the results obtained through the application of various analytical techniques to the sculptures under study. The aim of this chapter is to provide a detailed characterisation of the constituent materials, and the alteration products found on the metallic

surfaces, in order to contribute to a technical understanding of the works and to support the diagnosis of their conservation condition.

The methodologies employed, including EDXRF, XRD, SEM-EDS, OM and portable digital microscopy, were described in detail in the previous subchapter. Although not all techniques were applied to each sculpture, together they enabled the study to be approached at different levels: the direct observation of surface features, the analysis of the internal microstructure of the metal, and the identification of corrosion products. This comprehensive approach made it possible to characterise both the original alloy and the alteration processes affecting each work.

As this research is based on the analysis of specific sculptures located in different urban contexts, the results are organised by case study. Each sculpture is presented individually, and further structured into two main sections: alloy composition and corrosion products. The order of presentation prioritises sculptures for which both the alloy and corrosion layers were analysed, followed by those that were examined only in terms of alloy composition. Within each of these two groups, the case studies are arranged chronologically according to the date of casting. This approach allows for a more coherent integration and interpretation of the data obtained, and facilitates the correlation between material characteristics, deterioration phenomena and previous interventions identified in each work.

The results presented here form the basis for the comparative analysis and critical discussion to be developed in the following subchapter, where shared patterns and specific features observed across the analysed sculptures will be addressed.

5.3.1 Monumental Bust of Francisco de Almada e Mendonça

Analysis of the alloy

EDXRF was conducted on three points of the bust: the forehead (FA01), the left cheek (FA02), and the left armpit (FA03) (Fig. 5.6), selected for their accessibility and morphological relevance. The corresponding XRF spectra are presented in Appendix B.1. The results revealed a binary copper–tin alloy, with no zinc detected in any of the analysed points.

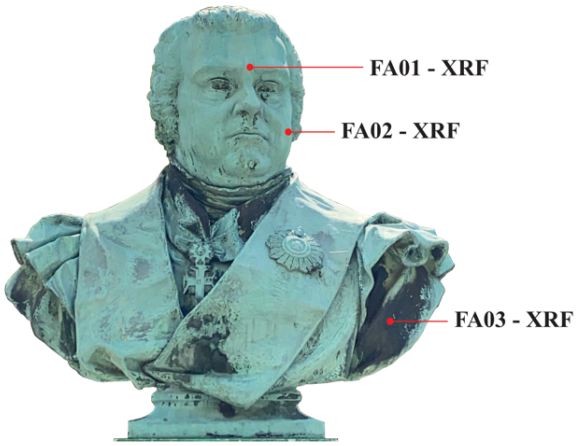


Fig. 5.6- EDXRF analysis zones on the monumental bust of *Francisco de Almada e Mendonça*.

As shown in Table 5.2, copper content ranged from 70.0% to 86.6%, while tin varied between 12.7% and 28.4%. These values indicate the use of a tin-rich bronze alloy, with higher concentrations than those typically found in standard formulations. It should also be noted that the unusually high tin levels may be partly due to the fact that the analyses were carried out without the removal of the corrosion layer, where the excess of tin oxide on the surface could have altered the results. Small amounts of lead, iron, arsenic and bismuth were

also detected, all below 0.6% by weight, possibly related to impurities in the original raw material or to period-specific casting practices.

Table 5.2 - Elemental composition (wt%) of the bust of *Francisco de Almada e Mendonça*, as determined by EDXRF. n.d.: not detected.

Bust of Francisco de Almada e Mendonça (1883, cast in 1885)								
Area	**Cu**	**Sn**	**Zn**	**Pb**	**Fe**	**As**	**Bi**	**Sb**
FA01	**86.6**	**12.7**	**n.d.**	n.d.	0.4	0.1	0.1	0.1
FA02	**70**	**28.4**	**n.d.**	0.3	0.2	0.4	0.6	0.1
FA03	**72.5**	**25.9**	**n.d.**	0.3	0.2	0.5	0.6	0.1

Analysis of the corrosion

The surface morphology was documented using portable digital microscopy, focusing on the lower rear section of the bust due to restricted access to the upper areas. Four representative zones were selected (Fig. 5.7a), in which significant differences in texture and colouration were observed (Fig. 5.7b).

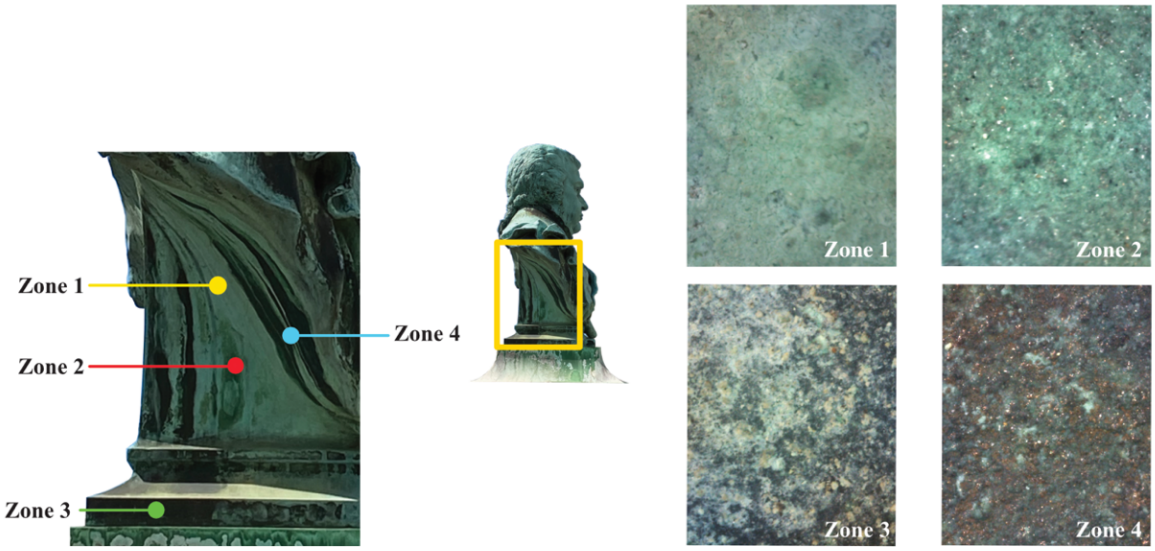


Fig. 5.7a Fig. 5.7b

Fig.5.7 - (a) Sampling areas observed using portable digital microscopy. (b) Images of the zones examined with portable digital microscopy.

Zone 1 displayed a pale green, smooth and homogeneous patina, with localised inclusions in dark green and beige tones. In Zone 2, a more intense green colour was observed, with a rough texture, waxy appearance, and bright spots that may correspond to silica minerals or surface reflections. These features suggest possible prolonged exposure to liquids, which may have intensified the hue and altered the original texture.

Zone 3 showed a dark, rough surface with remnants of pale green and beige patina, although it was not possible to determine whether the dark colour resulted from encrustation or leaching processes. Finally, Zone 4 exhibited a predominantly dark patina with a high degree of roughness, including dispersed inclusions in reddish-brown and intense green tones, along with bright points possibly related to silica minerals or localised exposure of the underlying metal.

Based on these observations, samples were collected from three areas of the bust and an additional point on the pedestal for analysis by XRD (Fig. 5.8). The sampling areas were

selected specifically due to their morphological and chromatic differences, previously identified through visual inspection and portable digital microscopy. The samples were extracted using a sterile scalpel and stored in Eppendorf™ tubes for laboratory analysis.



Fig. 5.8 - Sampling areas for XRD analysis on the bust of *Francisco de Almada e Mendonça*.

The results revealed the presence of minerals commonly associated with bronze corrosion in urban environments, including brochantite ($Cu_4SO_4(OH)_6$), antlerite ($Cu_3SO_4(OH)_4$) and atacamite ($Cu_2Cl(OH)_3$), found in varying combinations depending on the sampling zone (Table 5.3).

Table 5.3 - Minerals identified by XRD in the samples collected from the bust of *Francisco de Almada e Mendonça*. Full XRD spectra are provided in Appendix B.2.

Bust of Francisco de Almada e Mendonça (X-ray Diffraction)				
Sample	**Brochantite**	**Antlerite**	**Atacamite**	**Hydrated magnesium sulphite hydrate**
FA01	X			
FA02	X		X	X
FA03		X		
FA04	X			

Sample FA01 contained only brochantite, while FA02 revealed a more complex mixture composed of brochantite, atacamite and a hydrated magnesium sulphite compound. FA03 showed only antlerite, and FA04 again exhibited brochantite. This mineralogical distribution suggests differentiated microenvironmental conditions, possibly related to surface orientation, moisture retention or the selective deposition of airborne contaminants.

In particular, sample FA02-XRD, corresponding to one of the dark-patina zones, confirmed the presence of brochantite, atacamite and hydrated magnesium sulphite. This mineralogical configuration supports the hypothesis of localised exposure to specific contaminants, possibly linked to water runoff containing dissolved salts, and aligns with the morphological alterations previously observed in that same area.

5.3.2 Monumental Statue of King Afonso Henriques

The statue of King Afonso Henriques, located in the city of Guimarães, was the subject of a comprehensive study focused on the characterisation of its metal alloy, corrosion products, and microstructural features. The results obtained through EDXRF, XRD, metallography, and SEM-EDS were published in the journal *Heritage* (General-Toro et al., 2021) as part of this project. In the context of this thesis, those results are expanded and presented alongside the analysis of other sculptures.

Analysis of the alloy

EDXRF analyses were carried out on both the statue and the sword held by *King Afonso Henriques*, enabling a comparative examination of the alloy compositions and potential insights into production processes and post-casting alterations.

For the statue, five areas on the rear side were examined, including four distinct regions of the mantle and a fifth zone located on the base, over a representation of a wooden block (Fig. 5.9). These areas were chosen in response to the limited physical access available during the fieldwork, with the rear section being the only accessible zone at the time. Despite this constraint, the data obtained proved highly significant for the compositional study of the work. The corresponding XRF spectra for both elements are presented in Appendix B.3.

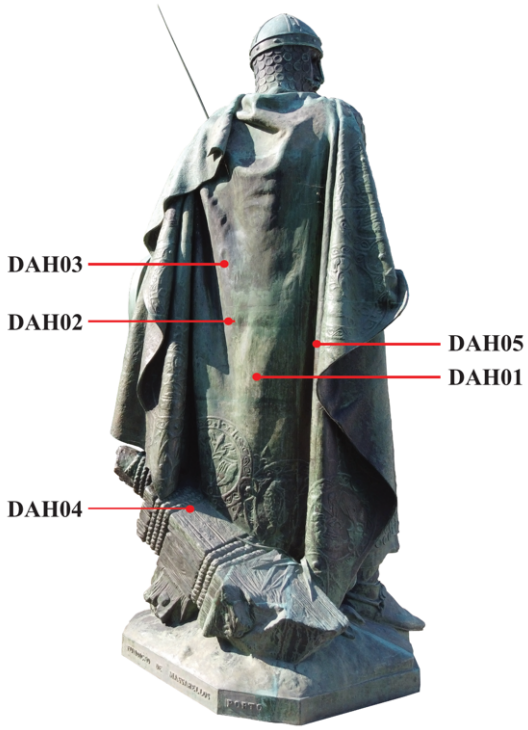


Fig. 5.9 - Surface areas of the statue of *King Afonso Henriques* analysed using EDXRF.

In all analysed points on the statue, a quaternary alloy consisting of copper, tin, zinc, and lead was detected, with copper as the dominant element, ranging from 63.7% (DAH01) to 88.2% (DAH05). Tin content varied between 7.2% and 20%, zinc from 1% to 9.9%, and lead between 0.8% and 2%, with trace elements such as iron, arsenic, and bismuth present in concentrations below 2% (Table 5.4).

Table 5.4 - Elemental composition (wt%) of the alloy in the statue of *King Afonso Henriques*. n.d.: not detected.

King Afonso Henriques – statue (1886, cast in 1887)								
Area	**Cu**	**Sn**	**Zn**	**Pb**	**Fe**	**As**	**Bi**	**Sb**
DAH01	**63.7**	**20**	**9.9**	**1.6**	2.1	1.3	0.5	n.d.
DAH02	**83.2**	**10.7**	**3.3**	**1.1**	0.5	0.9	0.2	0.1
DAH03	**88.1**	**7.2**	**2.2**	**0.8**	1	0.5	0.1	0.1
DAH04	**69.4**	**19.6**	**5.2**	**2**	1.2	2.1	0.5	0.2
DAH05	**88.2**	**7.8**	**1**	**1.6**	0.8	0.4	0.1	0.1

These compositional variations may be related to the fact that the sculpture was produced in separate sections using sand casting. As documented in Chapter 2, this process involves pouring the metal into independent moulds, which may lead to the use of different metal batches or variations in the alloy proportions across sections.

The data refined using the Monte Carlo algorithm (Table 5.5) made it possible to correct for potential distortions caused by surface layers, such as patinas or coatings. In general, an increase in copper values and a reduction in elements such as tin, iron and zinc were observed when compared to uncorrected EDXRF data (Table 5.4). For example, in area DAH01, copper content increased from 63.7% to 67.5%, while tin decreased from 20% to 17.5%. Zinc, in turn, rose from 9.9% to 12.2%, and iron was significantly reduced from 2.1% to levels below 0.1%.

Table 5.5 - Elemental composition (wt%) of the surface of the statue of *King Afonso Henriques*, obtained through EDXRF and refined using the Monte Carlo method. n.d.: not detected.

King Afonso Henriques – statue (Monte Carlo algorithm)						
Area	**Cu**	**Sn**	**Zn**	**Pb**	**As**	**Bi**
DAH01	**67.5**	**17.5**	**12.2**	**1**	1.3	0.5
DAH02	**84.1**	**10.9**	**3**	**1**	0.9	0.1
DAH03	**90.75**	**6.3**	**2**	**0.6**	0.3	0.05
DAH04	**75.3**	**13.5**	**6.6**	**2.1**	2.4	0.1
DAH05	**89.9**	**7.9**	**0.7**	**1.2**	0.3	n.d.

The spectrum corresponding to DAH01 also revealed the presence of barium, possibly linked to a dark brown artificial patina (Fig. 5.10), as well as a surface film attributed to an organic coating.

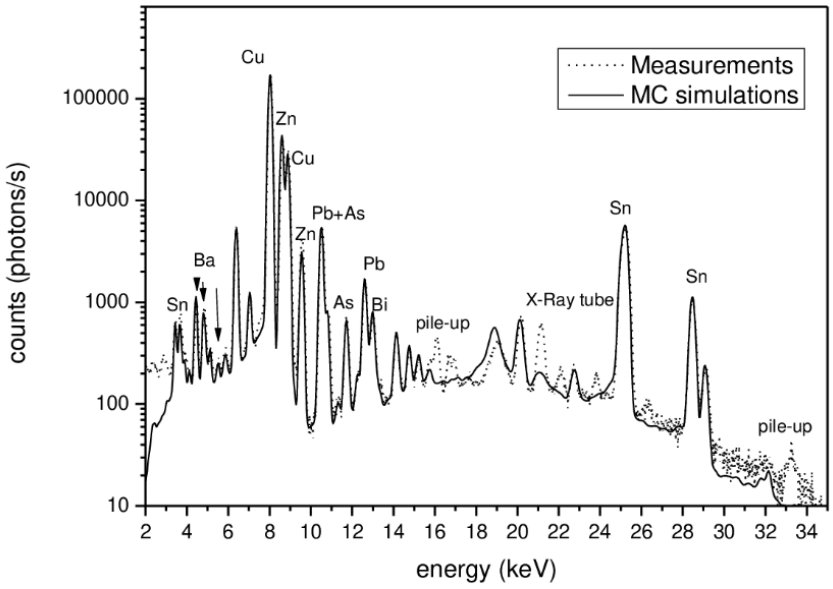


Fig. 5.10 - Analysis of area DAH01 via XRF spectroscopy, refined using the Monte Carlo method. Some peaks remain unadjusted, as they do not correspond to actual chemical elements but result from the pile-up phenomenon.

In parallel, twelve zones on the sword were analysed with the collaboration of the Directorate of the *Paço dos Duques de Bragança* (Fig. 5.11). The corresponding XRF spectra are presented in Appendix B.4.

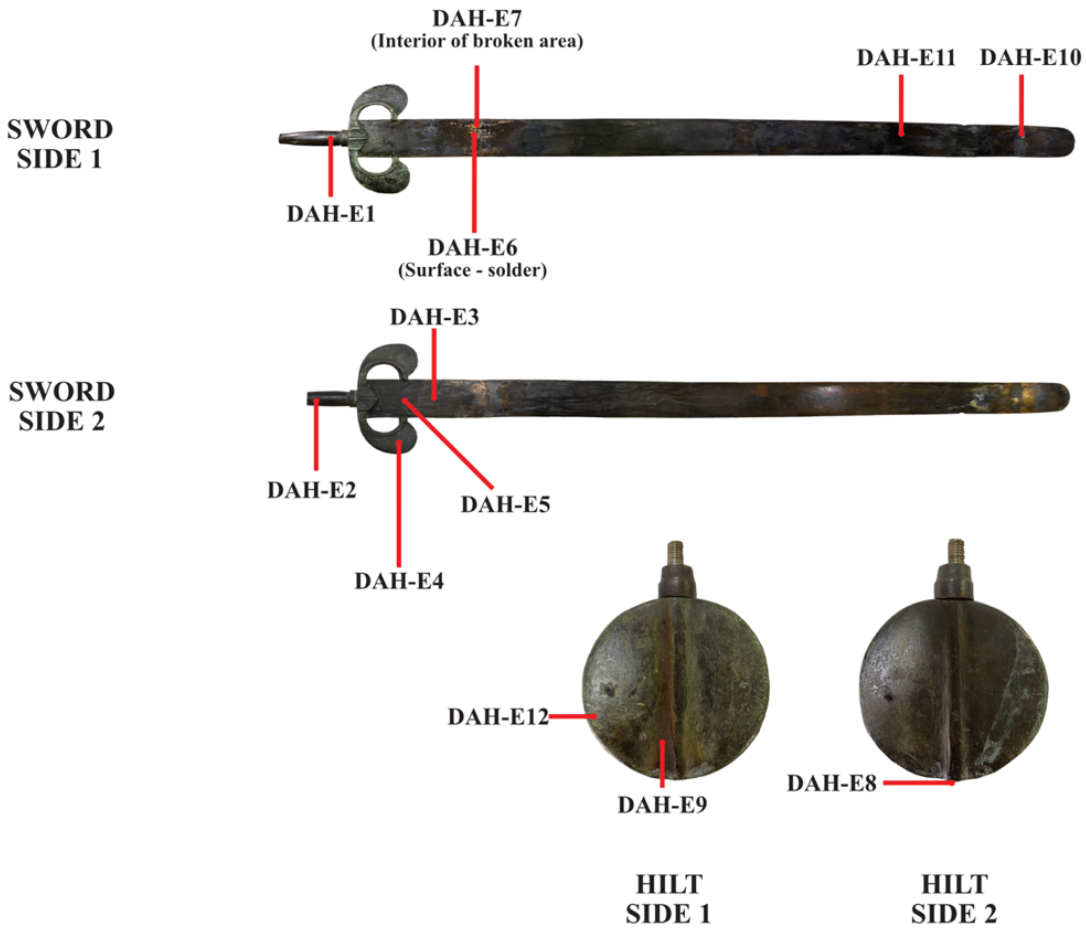


Figure 5.11 - EDXRF analysis zones on the sword of the statue of *King Afonso Henriques*.

The results also indicated an alloy with a generally higher copper content (83.9% to 91.7%) and lower tin (1.6% to 4.2%), as well as moderate levels of zinc (2% to 4.1%). The detailed results are shown in Table 5.6.

Table 5.6 - Elemental composition (wt%) of the sword of the statue of *King Afonso Henriques*.

King Afonso Henriques – sword (1886, cast in 1887)									
Area	**Cu**	**Sn**	**Zn**	**Pb**	**Fe**	**As**	**Bi**	**Sb**	**Ag**
DAH-E1	**91.4**	**3.1**	**3.5**	**1.0**	0.5	0.3	0.1	0.1	0.1
DAH-E2	**89.9**	**3.4**	**4.0**	**1.2**	0.7	0.4	0.1	0.1	0.1
DAH-E3	**84.1**	**4.2**	**3.8**	**1.4**	5.7	0.4	0.2	0.1	0.1
DAH-E4	**91.7**	**3.3**	**2.5**	**1.0**	1.0	0.3	0.1	0.1	0.1
DAH-E5	**83.9**	**4.2**	**4.1**	**1.4**	5.4	0.5	0.2	0.1	0.2
DAH-E6	**56.0**	**1.6**	**31.9**	**1.1**	0.3	6.5	0.8	1.1	0.7
DAH-E7	**68.6**	**2.0**	**25.1**	**3.0**	0.4	0.3	0.3	0.1	0.1
DAH-E8	**60.9**	**0.4**	**34.8**	**3.0**	0.7	n.d.	0.1	n.d.	n.d.
DAH-E9	**85.0**	**3.8**	**2.6**	**2.8**	5.0	0.4	0.2	0.1	0.2
DAH-E10	**76.7**	**1.8**	**18.9**	**0.5**	1.8	0.2	n.d.	n.d.	0.1
DAH-E11	**85.1**	**3.7**	**3.5**	**0.8**	6.3	0.2	0.1	0.1	0.2
DAH-E12	**89.4**	**3.6**	**3.2**	**2.2**	0.7	0.6	0.2	0.1	0.1

Trace elements, including iron, arsenic, bismuth, and silver, were particularly notable in areas with structural complexity or apparent surface alteration. Certain areas, such as DAH-E6, E7, E8, and E10, showed marked compositional deviations, with zinc levels reaching up

to 31.9% and copper decreasing to 56%. These anomalies were localised around joints and fastening points, suggesting the use of differentiated alloys for mechanical assembly or repairs, possibly as part of the original fabrication or later interventions.

Analysis of the corrosion

XRD analyses were undertaken to characterise the corrosion compounds present on both the statue of King Afonso Henriques and the sword held in its right hand, with the aim of identifying mineralogical patterns and understanding the stratigraphy of surface alteration products.

A total of ten samples were collected from the statue's surface, selected based on visual differences in colour and texture. These were grouped according to their location: samples labelled "AH" correspond to the rear of the sculpture (Fig. 5.12), while those designated "E" derive from frontal areas (Fig. 5.13). The distinction in nomenclature reflects the fact that these samples were gathered during different analytical campaigns. The XRD spectra are presented in Appendix B.5.

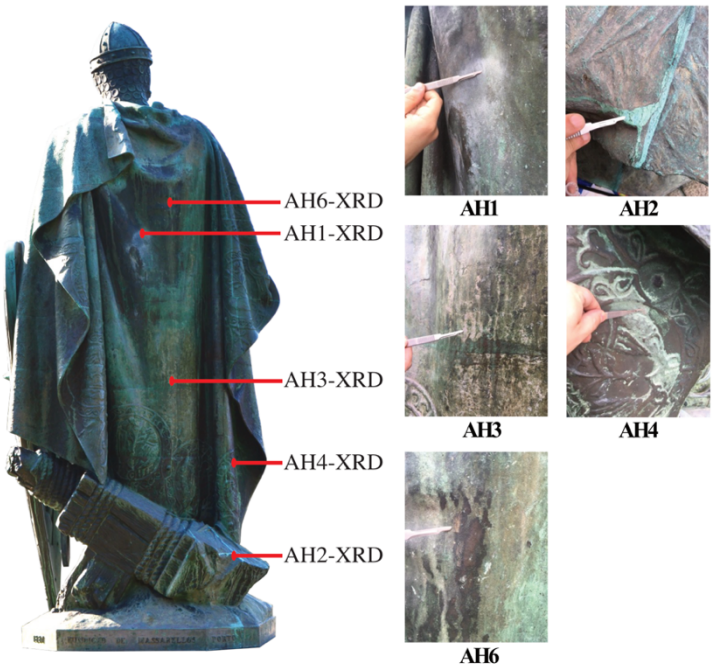


Fig. 5.12 - Areas of sample collection on the reverse (AH) side of the statue of *King Afonso Henriques* for XRD analysis.

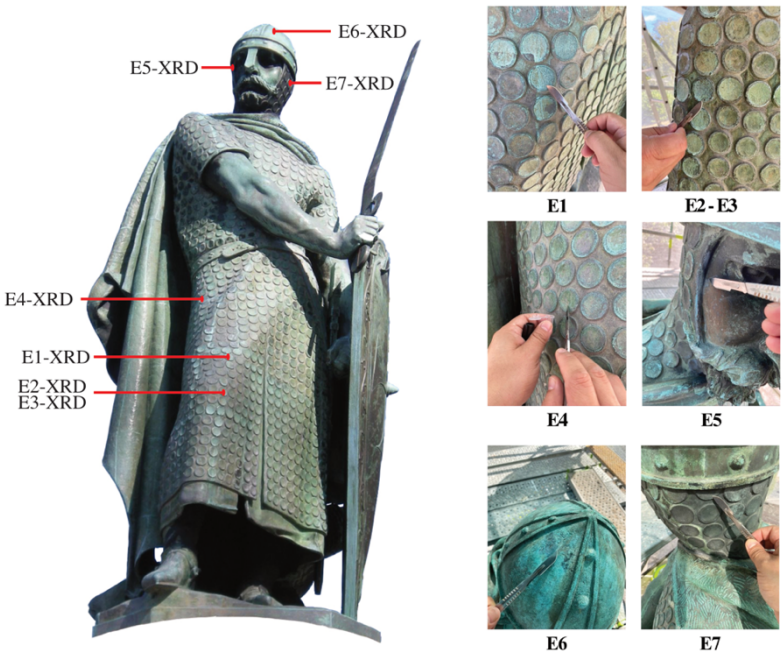


Fig. 5.13 - Sample collection areas on the front (E) side of the statue of *King Afonso Henriques* for XRD analysis. Sample E2 was taken from an area that later detached, while sample E3 originates from a recovered fragment.

The XRD data identified brochantite ($Cu_4SO_4(OH)_6$) as the most recurrent compound, present in nine out of the ten samples analysed. Cuprite (Cu_2O), a primary corrosion product, was detected in seven samples, confirming initial copper oxidation in several areas. Cassiterite (SnO_2) and posnjakite ($Cu_4(SO_4)(OH)_6 \cdot H_2O$) were identified in sample E2, corresponding to the frontal area of the sculpture, specifically in samples E5 and E6.

In contrast, quartz (SiO_2) was detected predominantly in samples taken from the rear of the sculpture, suggesting increased deposition of mineral particulates on those surfaces. In samples AH6, E6 and E7, a copper–tin phase tentatively identified as $Sn_{11}Cu_{40.5}$ was also detected. This identification should be treated with caution, as it may reflect remnants of the original alloy microstructure or limitations associated with phase identification in XRD analysis. Table 5.7 details the distribution of these compounds across the different samples.

Table 5.7 - Presence of minerals identified by XRD in the various samples collected from the statue of King Afonso Henriques. Samples with the prefix "AH" correspond to the rear of the sculpture, while those labelled "E" were taken from frontal areas.

King Afonso Henriques – statue (X-ray Diffraction)							
Sample	**Colour**	**Cuprite**	**Brochantite**	**Cassiterite**	**Posnjakite**	**Quartz**	**Copper - Tin**
AH1	White	X	X			X	
AH2	Light green/blue		X				
AH4	Pale green	X	X			X	
AH6	Pale green	X				X	X
E1	Green/Blue	X	X				
E2	Green/Blue	X	X		X		
E4	Yellow/green	X	X				
E5	Dark brown		X	X			
E6	Green/Blue		X	X			X
E7	Dark brown	X	X			X	X

In parallel, six XRD samples were taken from the sword, targeting areas that showed chromatic and textural heterogeneity (Fig. 5.14). The corresponding XRD spectra are presented in Appendix B.6.

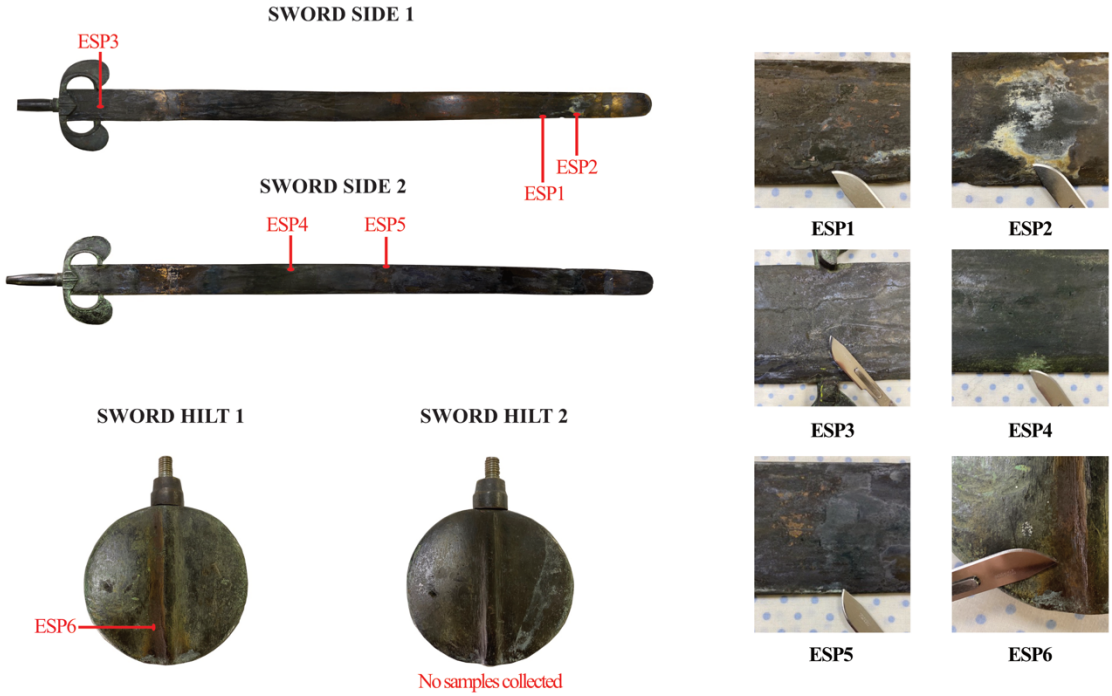


Fig. 5.14 - Location of the sampling areas on the sword of the statue of King Afonso Henriques, selected for XRD analysis.

The results revealed both similarities and notable distinctions when compared to the main body of the sculpture. Brochantite was again present in three of the sword samples (ESP2, ESP4, ESP5), reaffirming its prevalence as a dominant copper sulphate corrosion product in the ensemble. Posnjakite was identified in ESP2 and ESP5, accompanied by cuprite in ESP2 and tenorite (CuO) in ESP5, suggesting a more complex mineralogical assemblage in these zones, possibly resulting from localised microenvironmental conditions or stratification within the corrosion layers.

Quartz was also detected in two samples (ESP1 and ESP6). Notably, cassiterite, identified in the main statue, was absent from all sword samples. The complete results are presented in Table 5.8.

Table 5.8 - Presence of minerals identified by XRD in samples from the sword of the statue of *King Afonso Henriques*.

King Afonso Henriques – sword (X-ray Diffraction)						
Sample	**Colour**	**Cuprite**	**Brochantite**	**Posnjakite**	**Tenorite**	**Quartz**
ESP1	Dark brown	X			X	
ESP2	Light brown	X	X	X	X	
ESP3	Dark brown		X			
ESP4	Pale green	X	X			
ESP5	Dark brown		X	X	X	
ESP6	Brown		X			X

Microscopic Analysis of a Detached Fragment from the Statue of King Afonso Henriques

Although microscopy studies were not initially planned due to the inability to extract metal samples without compromising the integrity of the statue, a cleaning and protective intervention enabled access to previously unreachable areas, thereby enabling the collection of corrosion samples from the frontal area (Fig. 5.13). During this process, a small casting defect was identified in the surcoat, featuring a flat metallic protrusion measuring approximately 5 × 3 mm and 0.5 mm in thickness. Due to its fragility, the fragment detached easily with the aid of a scalpel. This sample, recorded as part of the frontal group of the sculpture samples (E3), was embedded in resin and used for both optical microscopy, SEM-EDS and SEM-FEG analysis.

Optical microscopy of the embedded sample revealed a predominantly dendritic alloy structure, with morphological variations indicative of uneven solidification dynamics. The

internal configuration of the metal is shown in Fig. 5.15a, while Fig. 5.15b shows globular inclusions located primarily in interdendritic regions and fissures.

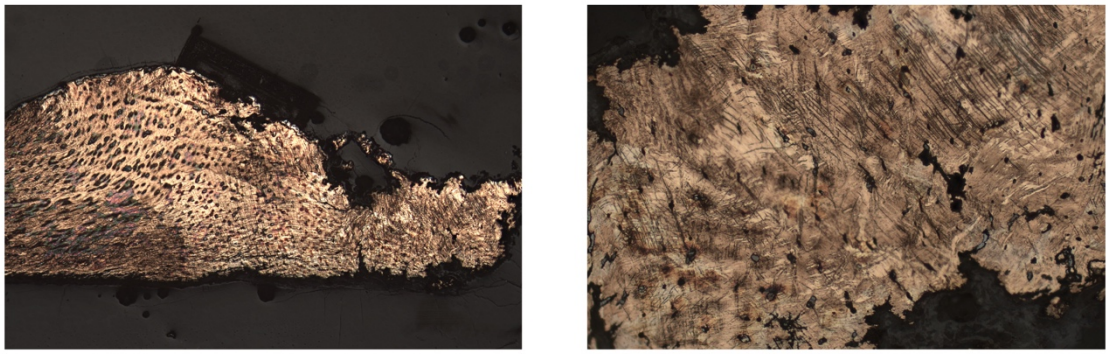


Fig. 5.15 - Metallographic microstructure of the metal fragment from the statue of *King Afonso Henriques* (Haute École Arc Ingénierie Laboratory, Le Locle, Neuchâtel, Switzerland). © Catherine Cséfalvay.

Observation under polarised light (Figs. 5.16 a and b) enhanced the visibility of crystalline orientations and phase distribution within the alloy. Numerous bright inclusions were identified throughout the microstructure, with a higher concentration near the surface. This region also displayed an irregular corrosion layer with a bluish-green hue. In Fig. 5.16b, the red frame highlights a surface accumulation of corrosion products or a potentially disaggregated secondary phase. Cracks and small discontinuities were also observed, possibly associated with internal stress within the metal or resulting from sample preparation.

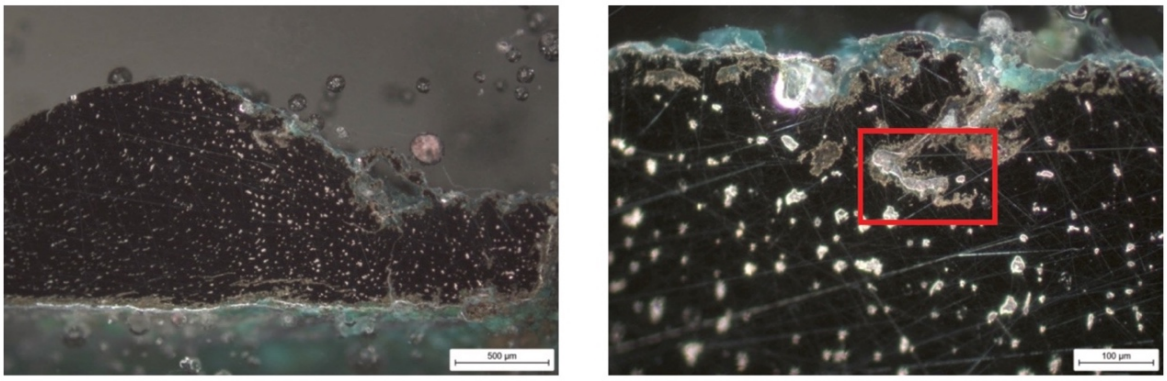


Fig. 5.16 - Fragment of the statue of King Afonso Henriques observed under polarised light microscopy (Haute École Arc Ingénierie Laboratory, Le Locle, Neuchâtel, Switzerland). © Catherine Cséfalvay.

The same fragment was subsequently analysed by SEM-EDS, allowing for a more refined characterisation of the alloy's microstructure and alteration patterns. SEM images revealed a metallic matrix composed of copper, tin and zinc, with bright globular lead inclusions dispersed throughout the microstructure (Fig. 5.17). Elemental EDS analysis also identified chlorine (Cl), silicon (Si), sulphur (S), and aluminium (Al) in the surface layers, suggesting a residual origin from casting sand. The elemental map for tin (Sn) showed surface enrichment, with higher concentrations near the surface (Fig. 5.18).

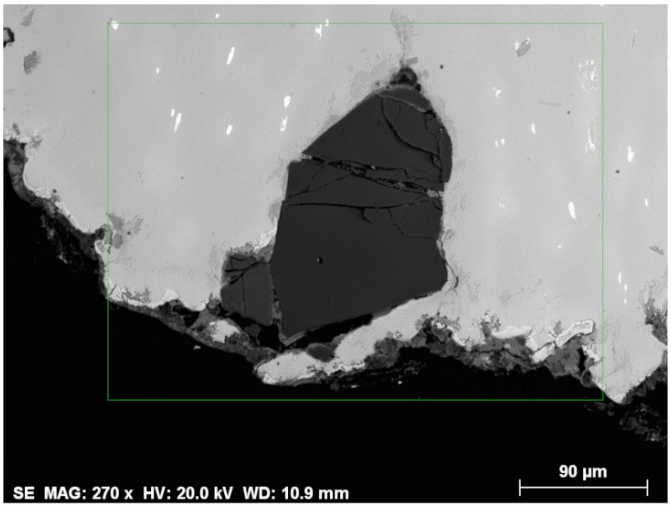


Fig. 5.17 - SEM image of the metal fragment (sample E3) from the statue of *King Afonso Henriques*, showing the alloy's microstructure and a quartz inclusion near the surface (HERCULES Laboratory, University of Évora). *Image from General-Toro et al. (2021).*

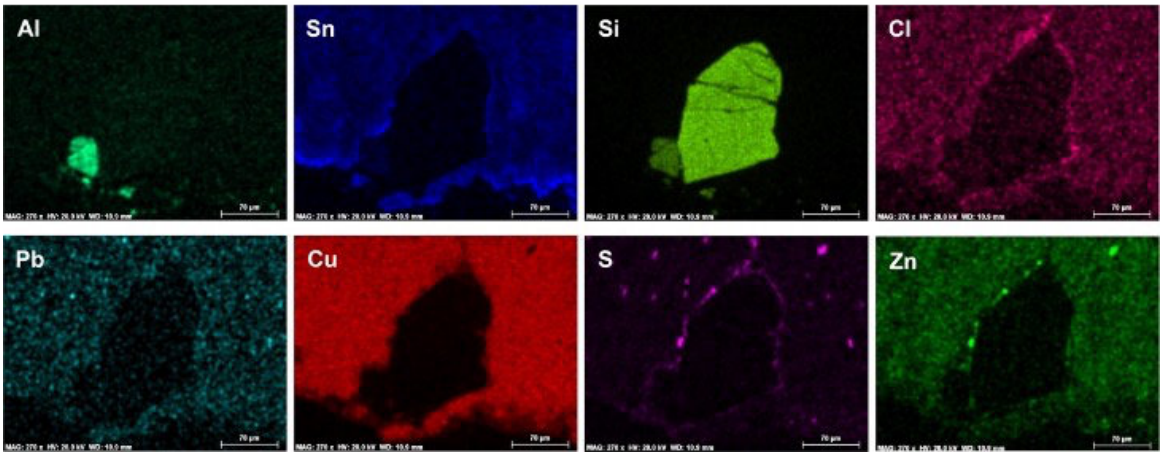


Fig. 5.18 - EDS map of the metal fragment (sample E3) from the statue of King Afonso Henriques, showing the distribution of Al, Sn, Si, Cl, Pb, Cu, S, and Zn (HERCULES Laboratory, University of Évora). *Image from General-Toro et al. (2021).*

SEM analysis also revealed evidence of intergranular corrosion, and cracking, both on the surface and at the interface between the metal and the patina (Fig. 5.19).

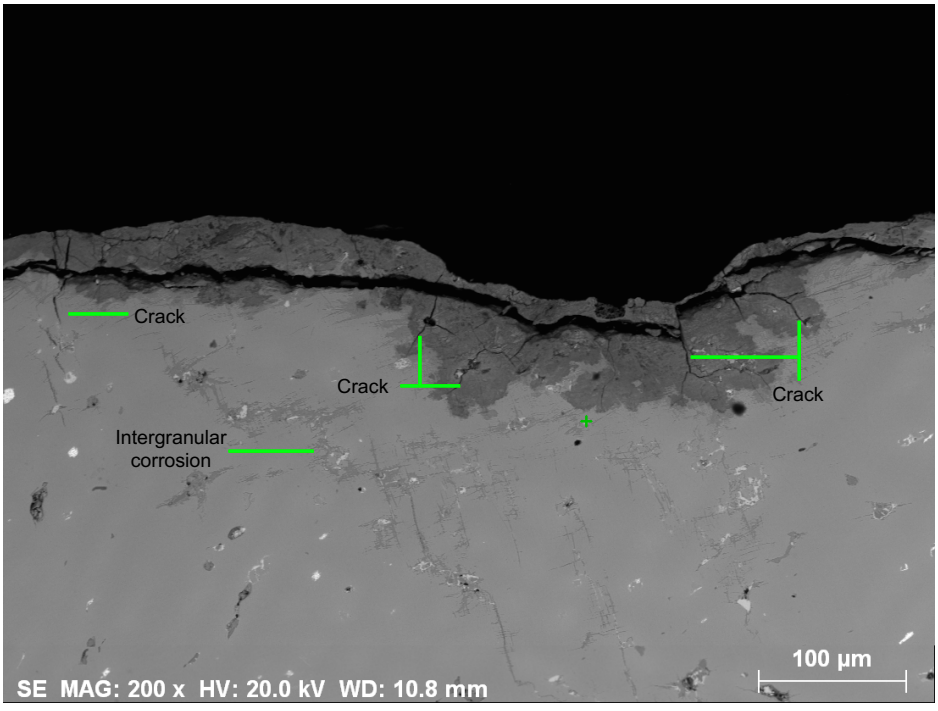


Fig. 5.19 - SEM image of sample E3 showing evidence of intergranular corrosion, and cracking. (HERCULES Laboratory, University of Évora, Portugal). *Image adapted from General-Toro et al. (2021).*

Finally, to evaluate the compositional transition between the metal core and the patina, an SEM-EDS *linescan* analysis was performed (Fig. 5.20). The results revealed higher copper concentration within the alloy core, decreasing progressively toward the surface. In contrast, tin displayed the opposite trend, with lower levels in the core and increasing concentration at the surface, consistent with the formation of tin oxide phases such as cassiterite. Zinc remained at low levels in both regions, while lead appeared in spherical inclusions, with a distribution inversely mirrored that of copper and tin.

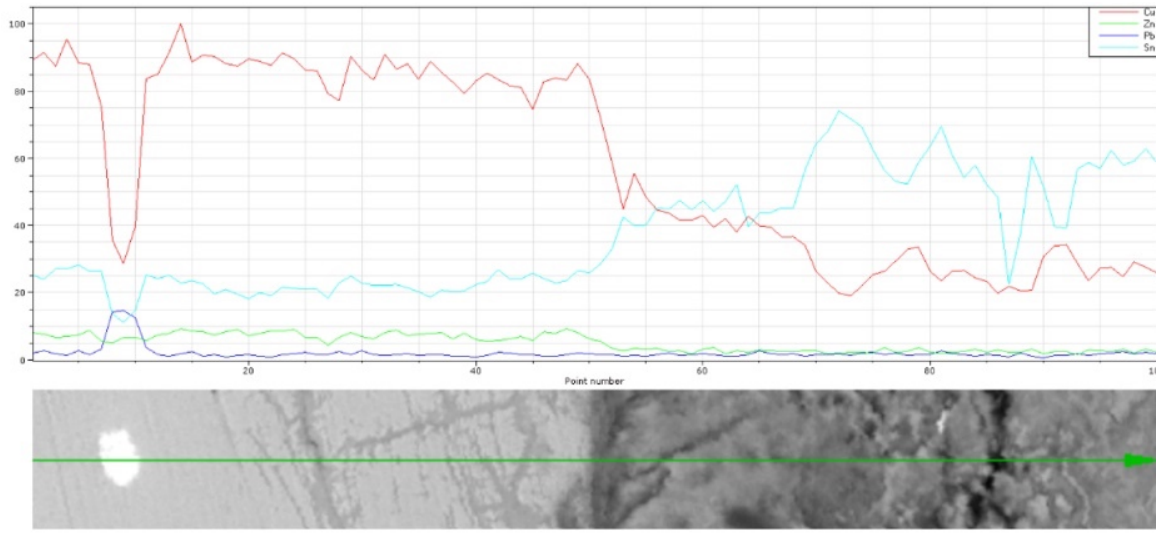


Fig. 5.20 - SEM-EDS *linescan* analysis of sample E3, showing variation in the concentration of copper (red), zinc (green), lead (blue), and tin (light blue) between the metal core and the patina (HERCULES Laboratory, University of Évora, Portugal). *Image from General-Toro et al. (2021).*

5.3.3 Sculpture of S. José

Analysis of the alloy

EDXRF analyses were conducted on four specific surface areas of the sculpture of *S. José*, each corresponding to different parts of the piece. The corresponding XRF spectra are presented in Appendix B.7. These areas are shown in Fig. 5.21, and the results are detailed in Table 5.9.

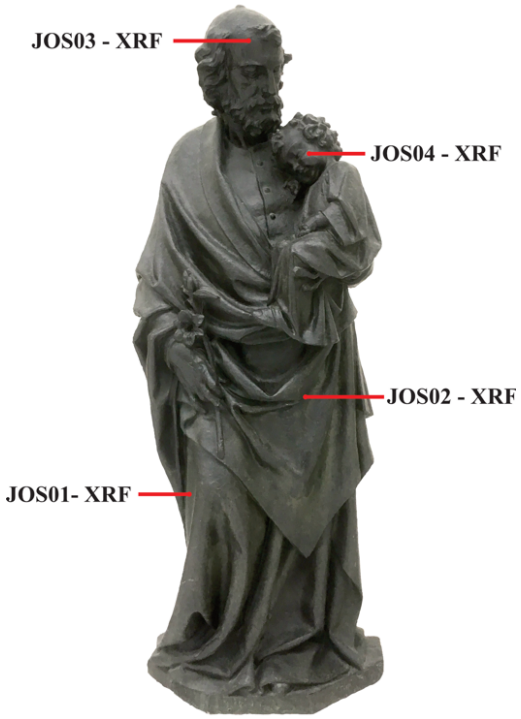


Fig. 5.21 - Areas analysed by EDXRF on the sculpture of *S. José*.

Table 5.9 - Elemental composition (wt%) determined by EDXRF on the sculpture of *S. José* (n.d.: not detected).

S. José (1880, cast between 1922 - 1927)							
Area	**Cu**	**Sn**	**Zn**	**Pb**	**Fe**	**As**	**Sb**
JOS01	**86.3**	**3**	**7.2**	**1.4**	1.8	0.1	0.1
JOS02	**86.2**	**3.1**	**8.6**	**0.8**	1.2	0.1	0.1
JOS03	**89.1**	**2.1**	**7.1**	**0.8**	0.9	0.1	n.d.
JOS04	**89.9**	**2.3**	**5.9**	**0.6**	1	0.1	n.d.

The results indicate that the sculpture was cast using an alloy with copper concentrations exceeding 86% in all samples. Zinc is the second most abundant component, ranging from 5.9% to 8.6%, followed by tin, present in concentrations between 2.1% and 3.1%. Lead is present in minor proportions, not exceeding 1.4%. Additionally, slightly elevated levels of iron (above 1%) were detected in three of the four areas, along with consistent traces of arsenic and antimony.

Analysis of the corrosion

Two samples from the sculpture of *S. José* were analysed, extracted from surface areas with visibly distinct characteristics (Fig. 5.22). The first sample (JOS01), corresponding to a green-toned patina, was provided by the Conservation Department of the MNSR and originated from the sculpture's right arm. The second sample (JOS02) was collected from beneath the visible foot, in an area with a dark brown patina of probable artificial origin. XRD spectra are presented in Appendix B.8. The results are summarised in Table 5.10.



Fig. 5.22 - Sampling areas for XRD analysis on the sculpture of *S. José*.

Table 5.10 - Minerals identified by XRD in the sculpture of *S. José*.

S. José (X-ray Diffraction)				
Sample	**Colour**	**Cuprite**	**Brochantite**	**Quartz**
JOS01	Green	X	X	X
JOS02	Dark Brown (artificial patina)	X		X

The analysis revealed the presence of cuprite (Cu_2O) in both samples, confirming the initial oxidation of the copper in the alloy. Brochantite ($Cu_4SO_4(OH)_6$), a corrosion product common in urban environments, was identified in sample JOS01. Quartz (SiO_2) was also detected in this sample, possibly originating from the deposition of airborne particles on the metal surface. In contrast, sample JOS02, which corresponds to an artificial patina, contained only cuprite and quartz, with no evidence of brochantite detected.

5.3.4 Sculpture of S. Joaquim

Analysis of the alloy

Three specific surface areas of the sculpture of *S. Joaquim* were analysed using EDXRF. The examined areas are shown in Fig. 5.23, the XRF spectra are presented in Appendix B.9 and the results are presented in Table 5.11.

The results show that the sculpture was cast with an alloy containing copper levels between 83.7% and 89.6%. Zinc occurs in amounts ranging from 4.5% to 6.8%, while tin varies between 2.6% and 4.9%. Lead appears only in small quantities, remaining below 1.2% in all samples. A markedly high iron concentration was recorded in sample JOA03 (4.5%), whereas in the other two areas, iron ranged from 1% to 1.8%. Stable trace amounts of arsenic and antimony were also detected.



Fig. 5.23 - Areas analysed by EDXRF on the sculpture of *S. Joaquim*.

Table 5.11 - Elemental composition (wt%) determined by EDXRF on the sculpture of *S. Joaquim* (n.d.: not detected).

S. Joaquim (1880, cast between 1922 - 1927)							
Area	**Cu**	**Sn**	**Zn**	**Pb**	**Fe**	**As**	**Sb**
JOA01	**89.6**	**2.6**	**5.8**	**0.8**	1	0.1	n.d.
JOA02	**87.3**	**4.9**	**4.5**	**1.2**	1.8	0.2	0.1
JOA03	**83.7**	**3.8**	**6.8**	**0.9**	4.5	0.1	0.1

Analysis of the corrosion

To complement the elemental analysis, XRD was performed on two samples from the sculpture of *S. Joaquim*, taken from areas with distinct surface characteristics (Fig. 5.24). The corresponding XRD spectra are presented in Appendix B.10. Sample JOA01 was collected from beneath the left foot, while sample JOA02, corresponding to a green patina on the right hand, was provided by the Conservation Department of the MNSR. The results are summarised in Table 5.12.



Fig. 5.24 - Sampling areas for XRD analysis on the sculpture of *S. Joaquim*.

Table 5.12 - Minerals identified by XRD in the sculpture of *S. Joaquim*.

S. Joaquim (X-ray Diffraction)							
Sample	**Colour**	**Cuprite**	**Atacamite**	**Posnjakite**	**Paraffin wax**	**Silicon phosphate**	**Barium chloride hydrate**
JOA01	Dark brown	X			X	X	X
JOA02	Green	X	X	X	X		

Both samples revealed the presence of cuprite (Cu_2O), as well as paraffin wax, which may be associated with previous conservation treatments. In sample JOA02, atacamite ($Cu_2Cl(OH)_3$) and posnjakite ($Cu_4(SO_4)(OH)_6 \cdot H_2O$) were also identified compounds commonly formed in urban environments under the influence of chlorides and sulphur compounds. Additionally, silicon phosphate (SiP_2O_7) and barium chloride hydrate ($BaCl_2 \cdot 2H_2O$) were detected. These may be related to environmental contamination, potentially exacerbated by the location of sample JOA01 in a less visible area of the sculpture, where the accumulation of airborne particles and surface residues is more likely.

5.3.5 Bust of João Marques de Oliveira

Analysis of the alloy

EDXRF analyses were carried out on four areas of the bust, as shown in Fig. 5.25. The results are presented in Table 5.13, and the XRF spectra are presented in Appendix B.11.



Fig. 5.25 - Areas analysed by EDXRF on the bust of *João Marques de Oliveira*.

Table 5.13 - Elemental composition (wt%) determined by EDXRF on the bust of *João Marques de Oliveira* (n.d.: not detected).

Bust of João Marques de Oliveira (1881, cast in 1926)								
Area	**Cu**	**Sn**	**Zn**	**Pb**	**Fe**	**As**	**Bi**	**Sb**
MO1	**80.8**	**6.8**	**7.3**	**1.1**	3.7	0.1	n.d.	0.1
MO2	**75.1**	**10**	**6.9**	**2.1**	5.5	0.2	0.1	0.1
MO3	**83**	**6.9**	**8**	**0.9**	1	0.1	n.d.	n.d.
MO4	**80.5**	**6.7**	**6**	**0.7**	5.9	0.1	n.d.	0.1

The data indicate that the sculpture is composed of a quaternary alloy, with copper concentrations ranging from 75.1% to 83%. Tin levels are comparatively high in relation to other sculptures from the same decade, reaching values between 6.7% and 10%. Zinc appears in steady proportions, from 6% to 8%, while lead varies between 0.7% and 2.1%.

Sample MO2, corresponding to the cheek of the bust, is particularly noteworthy, as it exhibits the lowest copper content and highest tin concentration among the areas analysed. Additionally, a markedly high iron content, approaching 6%, was detected in three of the four samples. Trace amounts of arsenic, bismuth, and antimony were also consistently present.

Analysis of the corrosion

Portable digital microscopy was employed to examine various areas of the bust of João Marques de Oliveira, as shown in Figure 5.26. In area 1, the surface revealed an artificial patina, whereas area 2 presented corrosion products characterised by bluish and whitish tones. Notably, in areas 3 and 3a, evidence of interaction between the metal and bird droppings was documented. This interaction resulted in a hardened surface marked by bluish and whitish deposits; alongside saline efflorescence typically associated with biological activity. In area 4, a slight reddish surface discolouration was observed, which may be indicative of oxide formation or prolonged environmental exposure.



Fig. 5.26 - Areas examined using portable digital microscopy on the bust of *João Marques de Oliveira*.

Given the thinness of the patina layer and the bust's location in a public space, the sampling for analytical purposes was necessarily minimal. Only a single corrosion sample could be discreetly collected, to avoid any visual impact on the artwork (Fig. 5.27). The results of the XRD analysis are summarised in Table 5.14, and the XRD spectra is presented in Appendix B.12.

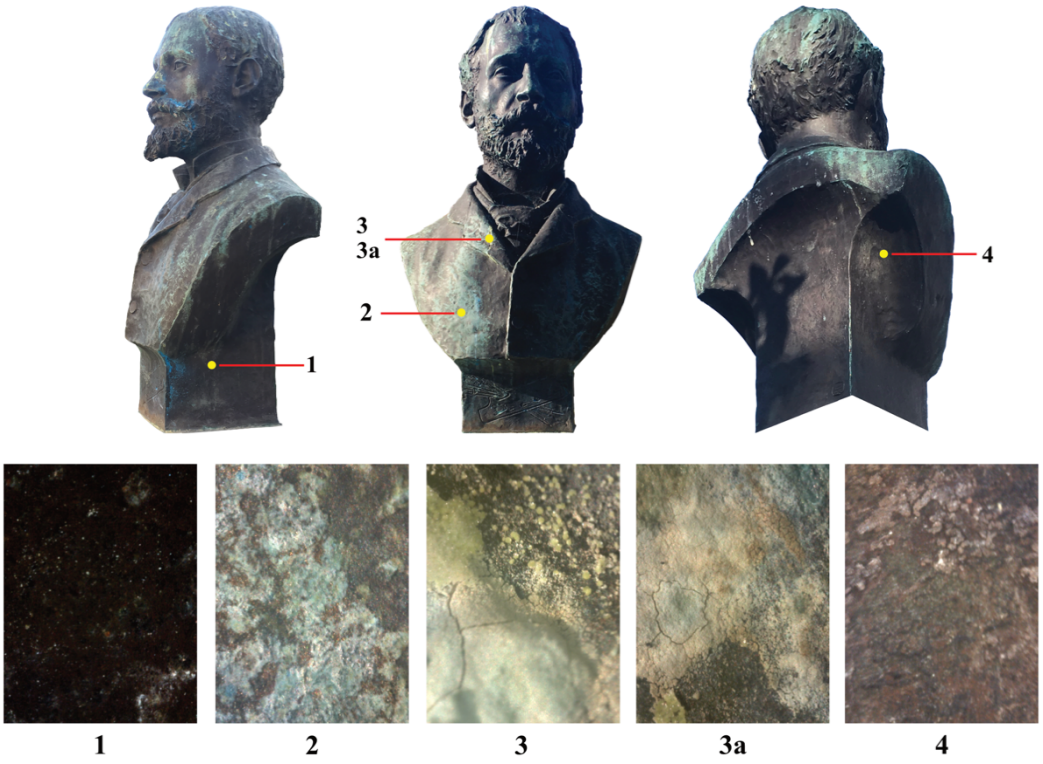


Fig. 5.27 - Sampling location for XRD analysis on the bust of *João Marques de Oliveira*.

Table 5.14 - Minerals identified by XRD in the bust of *João Marques de Oliveira*.

Bust of João Marques de Oliveira (X-ray Diffraction)			
Sample	**Colour**	**Cuprite**	**Cobalt copper tin**
MO01	Black	X	X

The XRD analysis confirmed the presence of cuprite (Cu_2O), a copper(I) oxide typically formed during the initial stages of copper corrosion. Additionally, a mixed cobalt–copper–tin compound was identified. This latter phase is likely associated with residual surface materials from an aerosol application, potentially linked to a past act of vandalism.

5.3.6 Figura Feminina

Analysis of the alloy

EDXRF analyses were carried out on four points of the sculpture *Figura Feminina*, as shown in Fig. 5.28. The results are summarised in Table 5.10, and the XRD spectra are presented in Appendix B.13.

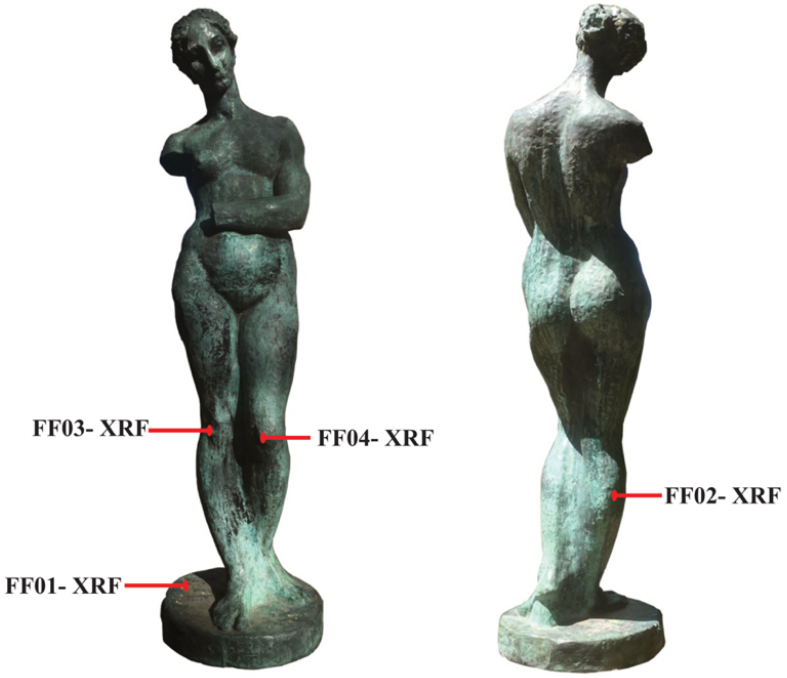


Fig. 5.28 - Areas analysed by EDXRF on the sculpture *Figura Feminina*.

Table 5.15 - Elemental composition (wt%) determined by EDXRF on the sculpture *Figura Feminina* (n.d.: not detected).

Figura Feminina (1867, cast in the 1965)								
Area	**Cu**	**Sn**	**Zn**	**Pb**	**Fe**	**As**	**Bi**	**Sb**
FF01	89.6	1.3	5.3	2.2	1.3	0.1	0.1	0.1
FF02	88.3	1.2	7.4	2.1	0.8	n.d.	0.1	n.d.
FF03	89	1	7.6	1.3	0.9	0.1	n.d.	n.d.
FF04	86.6	1	8.9	1.8	1.5	0.1	n.d.	0.1

The data indicate that the sculpture is composed of a quaternary alloy, with copper levels varying from 86.6% to 89.6%. Zinc is the second most abundant element, varying between 5.3% and 8.9%. Tin and lead were also detected, both in concentrations above 1%, with lead reaching up to 2.2% in certain areas. Low amounts of iron and trace quantities of arsenic, bismuth, and antimony were likewise recorded.

Analysis of the corrosion

Observations were carried out on nine areas of the sculpture *Figura Feminina* using portable digital microscopy. The results revealed marked surface heterogeneity, with noticeable variations in patina colour, corrosion morphology, and evidence of biological deposition (Fig. 5.29). In areas 1, 2, and 3, situated on regions with pale green patina, the appearance of green corrosion over a darker substrate was documented. These zones suggest active corrosion processes compromising previously stable patinated surfaces.

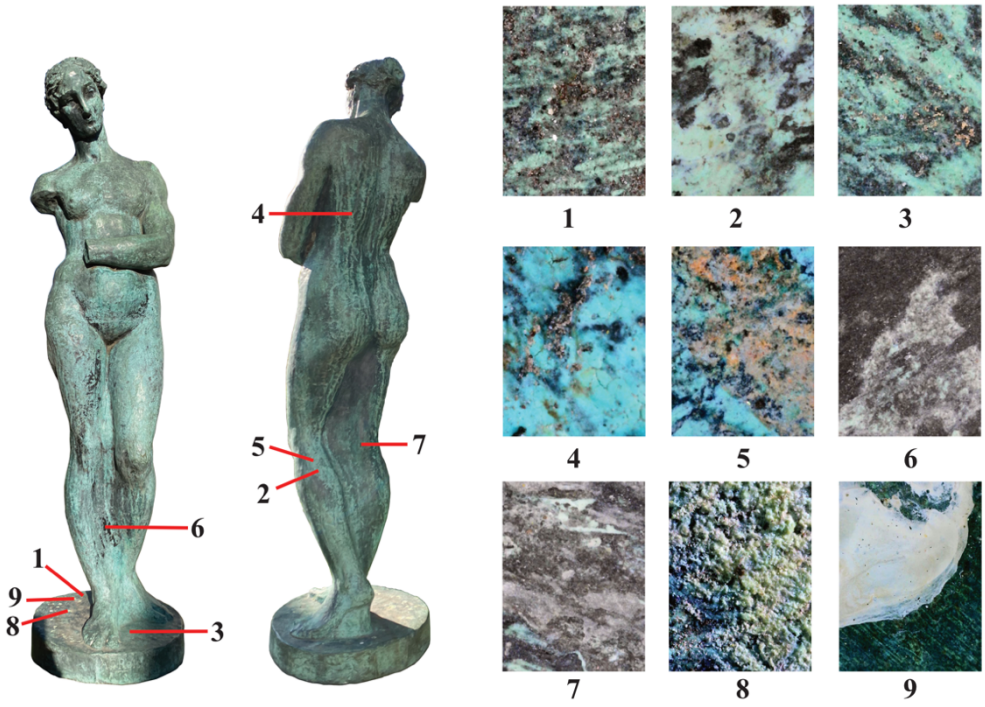


Fig. 5.29 - Areas examined with portable digital microscopy on the sculpture *Figura Feminina*.

In areas 4 and 5, bluish-green corrosion was observed, alongside a distinctive orange-toned region where the corrosion layer appeared to have been removed, revealing the underlying metal. This orange hue is consistent with the presence of cuprite (Cu_2O), a primary corrosion product of copper. Areas 6 and 7 displayed a dark surface film with emergent white growths. The phenomenon was especially pronounced in area 7, where the white formations were more developed and accompanied by traces of green corrosion, indicating localised salt accumulation likely influenced by microclimatic conditions.

Finally, areas 8 and 9 revealed traces of bird droppings. Area 8 showed visible surface alteration consistent with chemical interaction from faecal matter, indicative of advanced reactivity. In contrast, area 9 exhibited a more recent deposition, with no apparent impact on the underlying patina.

To further investigate the compositional differences in the patina, two samples were collected from zones exhibiting distinct chromatic characteristics (Fig. 5.30). Sample FF01 was taken from a green-toned area, while FF02 originated from a darker region. The results XRD analysis are presented in Table 5.16. and the XRD spectra are in Appendix B.14.

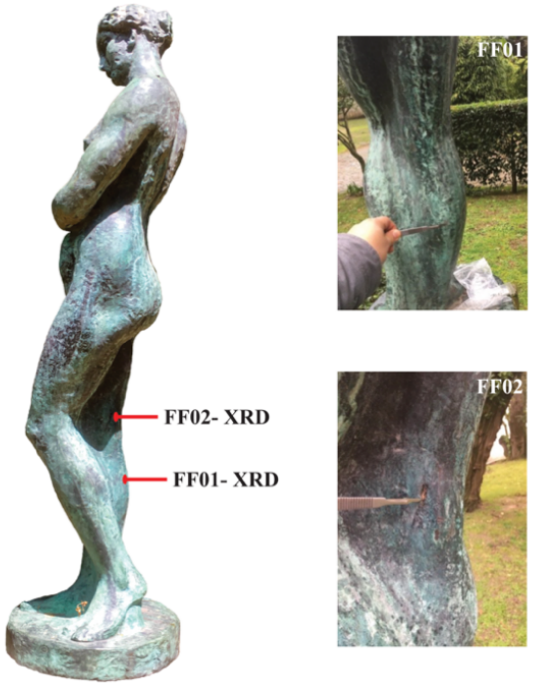


Fig. 5.30 - Sampling areas for XRD analysis on the sculpture *Figura Feminina*.

Table 5.16 - Minerals identified in the samples analysed by XRD from the sculpture *Figura Feminina*.

Figura Feminina (X-ray Diffraction)					
Sample	**Colour**	**Cuprite**	**Atacamite**	**Silicon phosphate**	**Silicon oxide**
FF01	Green	X	X		X
FF02	Dark	X	X	X	

XRD analysis revealed compositional variations between the two patina areas. In sample FF01, taken from the green-toned region, cuprite (Cu_2O), atacamite ($Cu_2Cl(OH)_3$), and silicon oxide (SiO_2) were identified. In sample FF02, extracted from the darker area, cuprite

and atacamite were also present, along with silicon phosphate. The occurrence of silicon-based compounds in both samples likely reflects the accumulation of airborne dust on the sculpture's surface.

5.3.7 Busto de Firmino

Analysis of the alloy

Three areas of the *Bust of Firmino* were analysed using EDXRF: the left cheek (FIR01), the right chest (FIR02), and the left rear side of the sculpture (FIR03), as shown in Fig. 5.31. The results are presented in Table 5.16, and the XRF spectra in the Appendix B.15.

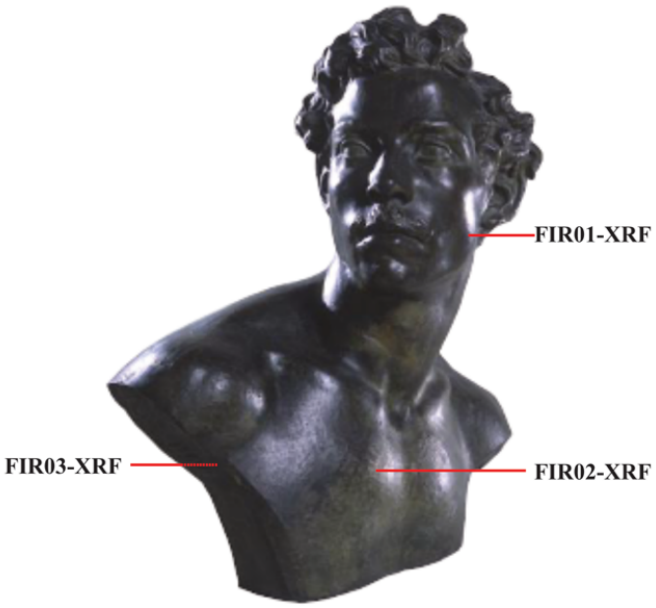


Fig. 5.31 - Areas analysed by EDXRF on the *Bust of Firmino*.

Table 5.17 - Elemental composition (wt%) of the *Bust of Firmino*.

Busto de Firmino (1867, cast between 1922 -1927)						
Area	**Cu**	**Sn**	**Zn**	**Pb**	**Fe**	**As**
FIR1	**87.8**	**3.1**	**7.7**	**0.8**	0.5	0.1
FIR2	**87.8**	**3**	**6.8**	**1.2**	0.9	0.1
FIR3	**89.3**	**2.9**	**6.3**	**0.8**	0.5	0.1

The results indicate a uniform elemental composition across the three areas analysed. Copper averages approximately 88%. Zinc is the second most abundant element, at around 7%, followed by tin at approximately 3%. Lead occurs in concentrations below 1% in most of the samples. In addition, trace amounts of iron and arsenic were consistently detected.

5.3.8 Academia – Homem Sentado

Analysis of the alloy

The sculpture *Academia – Homem Sentado* was analysed using EDXRF in three specific areas: the left knee (ACA01), the central right section of the back (ACA02), and the left surface of the seat (ACA03), as shown in Fig. 5.32. The results are detailed in Table 5.18. The XEF spectra is presented in Appendix B.16.

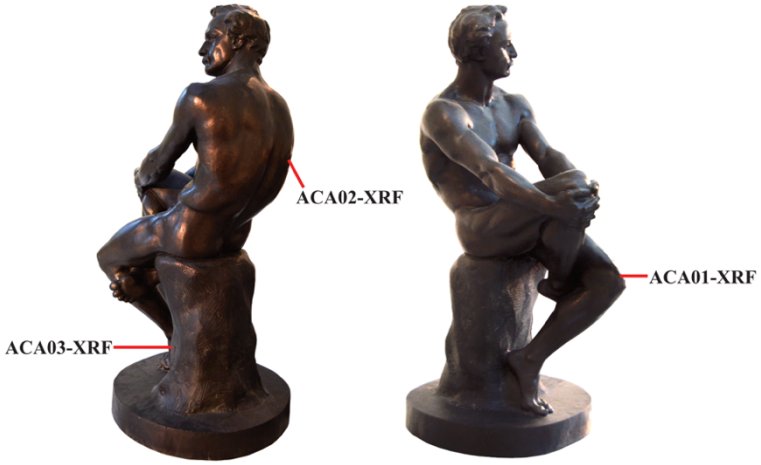


Fig. 5.32 - Areas analysed by EDXRF on the sculpture *Academia – Homem Sentado*.

Table 5.18 - Elemental composition (wt%) determined by EDXRF on the sculpture *Academia – Homem Sentado* (n.d.: not detected).

Academia – Homem sentado (1868, cast in 1927)								
Area	**Cu**	**Sn**	**Zn**	**Pb**	**Fe**	**As**	**Sb**	**Ni**
ACA01	**86.4**	**2.9**	**8.1**	**1.4**	0.8	0.2	0.1	0.1
ACA02	**90.1**	**2.2**	**6.2**	**0.7**	0.6	0.1	n.d.	0.1
ACA03	**88.1**	**2.9**	**7.4**	**0.7**	0.5	0.2	0.1	0.1

The results indicate that the sculpture is composed of an alloy with copper exceeding 86% across all areas and reaching 90.1% in ACA02. Zinc is the second most abundant element, varying between 6.2% and 8.1%, followed by tin, detected in concentrations from 2.2% to 2.9%. Lead remains below 1% in most samples, except in ACA01, where it reaches 1.4%. Minor quantities of iron, arsenic, antimony, and nickel were also identified in all areas.

5.3.9 O Pescador

Analysis of the alloy

The sculpture O Pescador was analysed using EDXRF in four specific areas: the left thorax (PES01), the upper part of the right leg (PES02), the right buttock (PES03), and the right wrist (PES04), as shown in Fig. 5.33. The results obtained are presented in Table 5.19, and the XRF spectra in Appendix B.17.

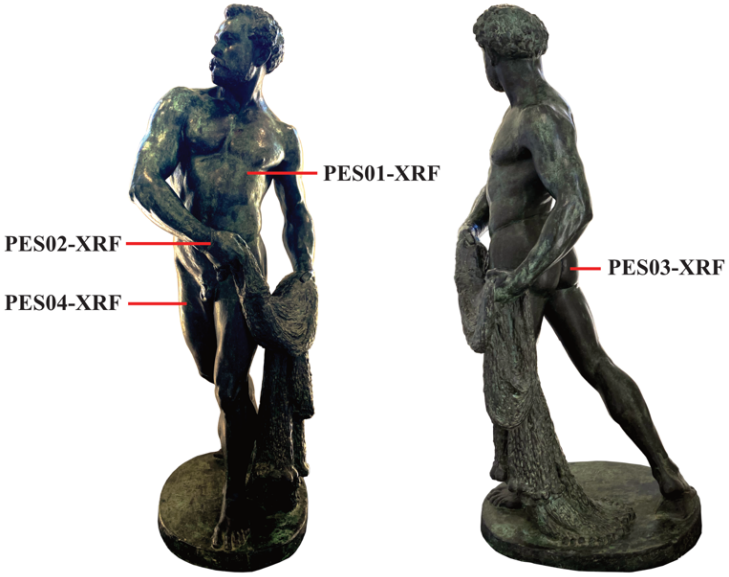


Fig. 5.33 - Areas analysed by EDXRF on the sculpture *O Pescador*.

Table 5.19 - Elemental composition (wt%) determined by EDXRF on the sculpture *O Pescador* (n.d.: not detected).

O Pescador (1870, cast between 1922 – 1927)									
Area	**Cu**	**Sn**	**Zn**	**Pb**	**Fe**	**As**	**Bi**	**Sb**	**Ni**
PES01	**87.5**	**3.9**	**6.7**	**1.1**	0.4	0.1	n.d.	0.1	0.2
PES02	**82.2**	**4.6**	**6.5**	**5.3**	0.8	0.2	0.1	0.1	0.2
PES03	**87.3**	**3.9**	**6.2**	**1.6**	0.4	0.2	n.d.	0.1	0.2
PES04	**85**	**2.7**	**9.3**	**1.4**	1.3	0.2	n.d.	0.1	n.d.

The results indicate that the sculpture is composed of a quaternary alloy, with copper above 82% in all areas and averaging around 85.5%. Zinc is the second most abundant element, varying from 6.2% to 9.3%, with the highest concentration recorded in PES04. Tin ranges between 2.7% and 4.6%, the lowest value also occurring in PES04. Lead falls between 1.1% and 1.6%, except in PES02, where it reaches a markedly higher level of 5.3%. Additional elements, including iron, arsenic, bismuth, antimony, and nickel, were detected in trace amounts.

5.3.10 Bust of Francisco Pinto Bessa

Analysis of the alloy

The bust of *Francisco Pinto Bessa* was analysed using EDXRF in three areas: the lower left section (BES01), the centre of the chest (BES02), and the upper part of the left shoulder (BES03). The areas analysed are shown in Fig. 5.34, and the results are detailed in Table 5.20. The XRF spectra are presented in Appendix B.18.

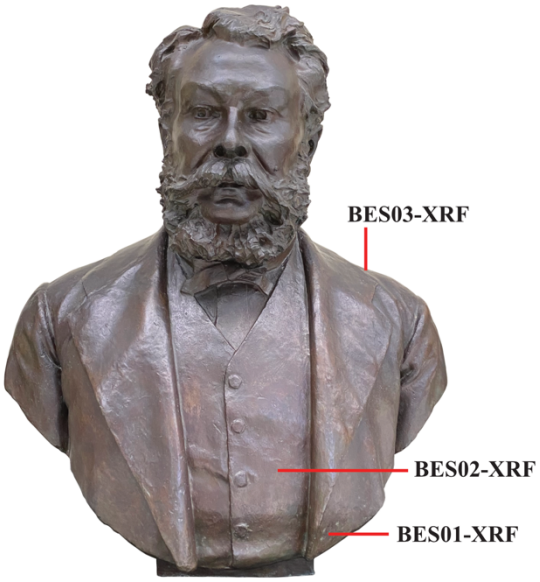


Fig. 5.34 - Areas analysed by EDXRF on the bust of *Francisco Pinto Bessa.*

Table 5.20 - Elemental composition (wt%) determined by EDXRF on the bust of *Francisco Pinto Bessa* (n.d.: not detected).

Bust of Francisco Pinto Bessa (1878, cast in 1940)								
Area	**Cu**	**Sn**	**Zn**	**Pb**	**Fe**	**As**	**Bi**	**Sb**
BES01	**80.2**	**5.2**	**5.6**	**8**	0.3	0.4	n.d	0.2
BES02	**86.4**	**4.9**	**3.1**	**4.7**	0.2	0.3	0.1	0.2
BES03	**86.9**	**3.9**	**5.1**	**3.4**	0.2	0.2	0.1	0.1

The results indicate that the bust is composed of a quaternary alloy, with copper averaging around 86% in two of the three areas analysed. In sample BES01, however, the copper content decreases to 80.2%. Zinc occurs in moderate concentrations, from 3.1% to 5.6%, while tin ranges between 3.9% and 5.2%. Lead content is comparatively higher than in other sculptures studied, varying from 3.4% to 8.0%, with the maximum value recorded in sample BES01. Minor quantities of iron, arsenic, bismuth, and antimony were also detected.

5.3.11 A Riqueza

Analysis of the alloy

EDXRF analysis was conducted on two areas of the sculpture *A Riqueza*: the left knee (RIQ01) and the front-right section of the base (RIQ02). The sampling locations are shown in Fig. 5.35, and the analytical results are presented in Table 5.21, and the XRF spectra are presented in Appendix B.19.



Fig. 5.35 - Areas analysed by EDXRF on the sculpture *A Riqueza.*

Table 5.21 - Elemental composition (wt%) determined by EDXRF on the sculpture *A Riqueza* (n.d.: not detected).

A Riqueza (1877, cast in 1954)								
Area	**Cu**	**Sn**	**Zn**	**Pb**	**Fe**	**As**	**Sb**	**Ni**
RIQ01	**79.7**	**1.8**	**16.3**	**0.9**	1	n.d.	0.1	0.2
RIQ02	**78.3**	**2.9**	**16.2**	**1.3**	0.9	0.1	0.1	0.1

The results show that the sculpture is composed of a quaternary alloy, characterised by a copper content below 80%, representing one of the lowest values recorded among the sculptures analysed in this study. Zinc occurs in notably high concentrations, exceeding 16% in both samples, while tin is comparatively low, ranging from 1.8% to 2.9%. Lead averages approximately 1.1%. Trace quantities of iron, arsenic, antimony, and nickel were also identified.

5.3.12 A Música

Analysis of the alloy

EDXRF analysis was conducted on three areas of the sculpture *A Música*: the right side (MUS01), the side of the base (MUS02), and the front of the base (MUS03). The specific sampling locations are shown in Fig. 5.36. The XRF spectra are presented in Appendix B.20, and the results are summarised in Table 5.22.



Fig. 5.36 - Areas analysed by EDXRF on the sculpture *A Música*.

Table 5.22 - Elemental composition (wt%) determined by EDXRF on the sculpture *A Música*.

A Música (1877, cast in 1957)					
Area	**Cu**	**Sn**	**Zn**	**Pb**	**Fe**
MUS01	**63.2**	**0.3**	**34.7**	**1.2**	0.5
MUS02	**65**	**0.4**	**32**	**1.8**	0.8
MUS03	**70.9**	**0.3**	**26.9**	**1.1**	0.6

The results indicate that the sculpture is composed of an alloy with a high zinc content, exceeding 26% in all areas analysed and reaching over 32% in MUS01 and MUS02. In contrast, copper levels are relatively low, remaining below 71%, with a minimum of 63.2% in MUS01. Lead is the third most abundant element, with concentrations ranging from 1.1% to 1.8%. Both tin and iron appear in minor proportions, consistently below 1%.

5.3.13 O Trabalho

Analysis of the alloy

To assess the metallic composition of the sculpture *O Trabalho*, EDXRF analysis was carried out on three selected areas: the right knee (TRA01), the lower part of the garment at the height of the left leg (TRA02), and the cloth held by the figure, on the rear side near the base (TRA03). The selected sampling points are illustrated in Fig. 5.37, the XRF spectra are presented in Appendix B.21, and the results are summarised in Table 5.23.

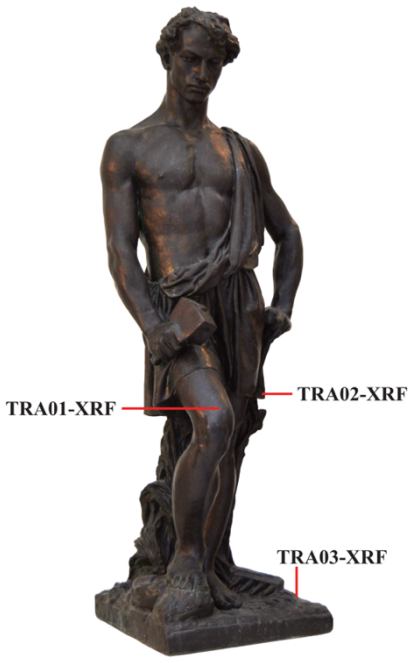


Fig. 5.37 - Areas analysed by EDXRF on the sculpture *O Trabalho*.

Table 5.23 - Elemental composition (wt%) determined by EDXRF on the sculpture *O Trabalho*.

O Trabalho (1876, cast in 1959)									
Area	**Cu**	**Sn**	**Zn**	**Pb**	**Fe**	**As**	**Bi**	**Sb**	**Ni**
TRA01	**83.7**	**4.3**	**7.9**	**3.1**	0.6	0.1	0.1	0.1	0.2
TRA02	**84.9**	**4.8**	**5.9**	**3.5**	0.4	0.1	0.1	0.2	0.1
TRA03	**81.2**	**3.5**	**11.3**	**2.6**	0.8	0.2	0.1	0.2	0.1

The data indicate that the sculpture is composed of a quaternary alloy, with copper levels above 81% and reaching 84.9% in TRA02. Zinc is the second most abundant element, with a particularly high concentration in TRA03 (11.3%). Tin occurs in amounts between 3.5% and 4.8%. Lead shows comparatively elevated values, exceeding 3% in two of the analysed areas. Trace quantities of iron, arsenic, bismuth, antimony, and nickel were also identified in all samples.

5.4 SYNTHESIS OF THE ANALYSIS

5.4.1 Analysis of the alloy

Sculptures Cast in the Late 19th Century

Compositional analyses conducted via EDXRF on the bust of *Francisco de Almada e Mendonça* (1883, cast in 1885) and the statue of King Afonso Henriques (1886, cast in 1887) revealed marked differences in their chemical profiles, even though they were produced only a year apart.

This contrast can be attributed to several factors. On the one hand, technical aspects such as the casting method and the location of the foundries, in Lisbon and Porto, likely played a role. On the other, these variations also reflect the technological limitations of the late 19th-century Portuguese context, where many industrial workshops were geared toward iron casting and lacked specialisation in copper alloys.

The bust of *Francisco de Almada e Mendonça* exhibits a binary alloy of copper and tin, with high tin content reaching up to 28.4% in some of the analysed areas, and no detectable presence of zinc. It should be considered, however, that such elevated tin values may be partly explained by the fact that the analyses were carried out without the prior removal of the corrosion layer. This formulation qualifies as high-tin bronze (Meeks, 1993; A. M. Pollard et al., 2018), known for its hardness and resistance to corrosion, although also for its greater brittleness.

Bronze is considered high-tin when it contains between 19% and 27% tin, a factor that decisively influences its mechanical properties, including increased hardness and fragility (Meeks, 1993).

The casting technique employed for this bust remains unidentified. A thick corrosion layer covers the surface, and access to the object is limited. These conditions prevent visual identification of the casting process, whether it was lost-wax or sand casting. No archival documentation has surfaced to clarify this aspect either.

This uncertainty is significant. If sand casting was indeed used, a method still employed today for bust production, then the observed variation in copper and tin ratios across different areas could reflect separate castings made at different times or under varying technical conditions.

Alternatively, some of the compositional disparity might stem from the progressive loss of tin in certain zones, caused by corrosion processes that gradually converted the element into secondary compounds.

Copper–tin alloys, such as that found in this sculpture, are characterised by high plasticity, structural integrity, mechanical strength, and exceptional durability in saline or marine environments (Jabłońska et al., 2019). Higher tin content enhances casting fluidity, sliding efficiency, and corrosion resistance while reducing shrinkage and hydrogen solubility. However, these advantages are offset by decreased tensile strength and impact resistance, and increased hardness (Nadolski, 2017).

The historical use of copper–tin alloys with low or undetectable traces of zinc is well-documented. Such alloys were widespread in Antiquity and remained prevalent through the 17th to 19th centuries, especially in cast items like artillery, musical instruments, and household objects (Barinaga, 1874; Coquilhat, 1855; Jabłońska et al., 2019; Leguina, 1907; Magne, 1917; Park et al., 2009; Peláez, 2003; Privat-Deschanel & Focillon, 1877; Slamet et al., 2021). High-tin bronze, in particular, played a crucial role in the manufacture of bells and mirrors, valued both technically and culturally (Meeks, 1993; Privat-Deschanel & Focillon, 1877; Saraiva et al., 2022; Vannoccio, 1572; Yokota et al., 2003).

In contrast, the statue of King Afonso Henriques was cast using a quaternary alloy of copper, tin, zinc, and lead. This type of formulation closely resembles those used in 20th-century

bronze sculpture, marking a significant shift in metallurgical practices between the two commissions (Ganio et al., 2014; É. Lebon, 2019; Pouyet et al., 2019; Randall, 2016).

The elevated zinc content in certain areas may reflect deliberate choices aimed at improving alloy fluidity, casting precision, and tensile strength. Meanwhile, small amounts of lead and arsenic may have been added intentionally to enhance machinability or may simply derive from material impurities.

The observed compositional variation likely stems from several converging factors. Firstly, the statue was produced using sand casting, a method that allows large works to be cast in separate segments and then assembled. As a result, each section may have been cast on different days, with slight differences in metal batches explaining the variations in copper, tin, and zinc.

Secondly, the foundry itself may have played a role. The Massarelos foundry, known primarily for ironwork, probably lacked extensive experience in bronze casting. This could have led to reduced control over alloy consistency and homogeneity. The combined effect of these technical and logistical limitations aligns with the observed analytical data.

Further insight was gained through Monte Carlo corrections applied to the elemental data, allowing for a refined estimation of patina thickness based on background shape and fluorescence attenuation (Brunetti, Golosio, Melis, et al., 2015; Brunetti, Golosio, Schoonjans, et al., 2015; General-Toro et al., 2021). This correction showed a notable reduction in iron content, likely attributable to superficial products such as artificial patina (Pouyet et al., 2019). The presence of barium in the outer layer further supports this hypothesis, suggesting the application of a dark artificial patina during finishing.

Metallographic and SEM-EDS analyses conducted on a fragment extracted during conservation revealed key structural data about the statue's alloy. The microstructure displayed a well-defined dendritic pattern, indicative of cast bronze.

Globular lead inclusions were found throughout the metal, particularly in interdendritic spaces and fissures. These correspond to typical micro-porosities resulting from the

solidification process. As higher melting elements solidify, the remaining molten lead flows into cavities and becomes trapped within the alloy matrix (Chiavari et al., 2007; General-Toro et al., 2021; Non-Ferrous Founders' Society & Copper Development Association, 1994).

The SEM analysis also identified intergranular corrosion, and cracking of the corrosion layer. These phenomena, observed at the surface and metal–patina interface, point to ongoing or historical deterioration.

Elemental mapping revealed silicon, chlorine, sulphur, and aluminium concentrated near the surface. These are likely residues from the sand mould, such as embedded quartz grains, one of which is visible in the SEM imagery. These findings offer insights into the production conditions and casting practices.

The statue's sword, also analysed, presents a different scenario. Assembled from multiple components, some removable, and having undergone repairs following vandalism, the sword exhibits a broader range of alloy compositions. Areas near joints or soldering points show higher zinc and lower copper levels, possibly reflecting the use of structurally tailored bronze alloys or recent restoration materials.

By contrast, original elements of the sword, such as the hilt and pommel, retain a more stable composition, similar to the alloy used in the statue itself. This contrast highlights how functional and restorative requirements can lead to noticeable compositional variations within the same object

The comparison between the statue and its sword underscores these distinctions. Although both elements share a quaternary copper–tin–zinc–lead base, the statue displays greater internal consistency. The sword's more heterogeneous profile likely reflects its structural complexity, the specific function of its components, and its restoration history. These observations reinforce how technical demands influence alloy selection, even within a single commission.

Sculptures Cast in the 1920s

The sculptures cast between 1922 and 1927, including *S. José*, *S. Joaquim*, *Bust of Firmino*, *Academia, Homem Sentado*, and *O Pescador*, display a remarkable consistency in their elemental composition. Archival records confirm that several sculptures by António Soares dos Reis were cast at the Adelino Sá Lemos foundry in Porto, under commission from the EBAP. Although the works examined in this study are not explicitly referenced in those documents, the chronological and technical alignment strongly suggests that they were also produced at that foundry.

In all cases, the sculptures are composed of copper-based alloys with varying amounts of tin, zinc, and lead, as well as trace elements such as iron, arsenic, antimony or nickel. While the precise values differ across zones and sculptures, a relatively uniform formulation can be observed. Copper content ranges from 82% to 90%, tin from 2% to 5%, and zinc between 5% and 9%. These proportions suggest the use of a standard bronze alloy tailored to the technical and aesthetic requirements of the time, potentially developed through recurring foundry practices within the same workshop.

Lead is consistently present across all sculptures, typically not exceeding 1.6%, and serves a functional purpose in enhancing the fluidity of the alloy. However, *O Pescador* presents an exception. In sample PES02, taken from the right wrist, an area showing a casting defect, lead was measured at 5.3%. This anomaly may reflect a targeted adjustment to improve castability in a difficult-to-reach section, or from a localised segregation of lead during the cooling process.

Variations in trace elements such as iron, arsenic, antimony, or nickel are not always straightforward to attribute. In the case of iron, as previously noted in the Afonso Henriques statue, its detection might be influenced by the presence of patina or other surface coatings, potentially skewing EDXRF results. Arsenic, on the other hand, may have been deliberately added to improve mechanical performance, such as corrosion resistance and high-

temperature strength (H. Zhang et al., 2021), or it may occur as a natural impurity in the raw materials (Lechtman, 1996).

A unique case among the 1920s sculptures is the bust of João Marques de Oliveira, cast in 1926 by the Hébrard foundry in Paris. This work exhibits a markedly different composition, with tin levels reaching up to 10%, considerably higher than those observed in contemporary Portuguese sculptures. Copper concentrations are slightly lower, ranging from 75.1% to 83%.

Another distinctive feature is the consistently high iron content, particularly in two of the analysed samples. While this may partially stem from surface residues or patination, the levels recorded stand out when compared to other works from the same period.

The pronounced disparity in copper and tin proportions observed in sample MO2 may be attributed to a lack of homogeneity during the casting process or to a redistribution of tin towards the interface with the patina, where cassiterite (SnO_2) typically forms. However, this compound could not be identified in the sample, likely due to recent cleaning following acts of vandalism, an intervention that removed much of the natural patina and the layers where such corrosion products usually occur.

As outlined in Chapter 1, the Hébrard foundry which specialised in lost-wax casting and catered to a more discerning artistic clientele within the French upper class. This context helps explain the use of more complex compositions, adapted to technical standards different from those observed in Portuguese sculptures, which were more closely tied to institutional commissions and more standardised casting methods.

This comparison supports the broader idea that production context, in both technical and social terms, directly influences the formulation of sculptural alloys. While the Portuguese works reflect more homogeneous practices linked to local industrial foundries, the bust cast in Paris stands as an example of greater sophistication in both technique and alloy composition, likely rooted in the refined expertise of art foundries serving a high-end market. It also reinforces the notion, already observed in the preceding case studies, that alloy

formulation was closely shaped by functional requirements, aesthetic expectations, and the level of specialisation in each production context.

Sculptures Cast in the Mid- 20th Century

The sculptures cast between 1940 and 1965: *Bust of Francisco Pinto Bessa* (1940), *A Riqueza* (1954), *A Música* (1957), *O Trabalho* (1959), and *Figura Feminina* (1965), exhibit considerable compositional diversity, in contrast to the greater homogeneity observed in works produced in previous decades. This variability may be associated with changes in technical casting practices as well as with differing availability of materials used in the formulation of alloys.

The *Bust of Francisco Pinto Bessa*, cast in 1940 by commission of the Comissão dos Centenários and produced by the Abreu foundry in Lisbon, presents a quaternary alloy with copper concentrations ranging from 80.2% to 86.9%. Unlike the earlier sculptures, this piece stands out for its high lead content, with levels reaching 8% in one of the analysed areas (BES01), a significantly elevated value compared to works from previous decades. Zinc, on the other hand, remains within moderate ranges (3.1% to 5.6%), while tin is present at 3.9% to 5.2%. This type of formulation may reflect an alloy optimised for casting efficiency, reduced melting point, and improved machinability; characteristics enhanced by the presence of lead (Kuyucak & Sahoo, 1996).

The sculptures *A Riqueza* (1954), *A Música* (1957), and *O Trabalho* (1959), all cast by the José Castro Guedes foundry under commission from the MNSR, share certain compositional similarities. *A Riqueza* and *A Música* exhibit alloys with notably high zinc levels (over 30% in some samples of *A Música*, and around 16% in *A Riqueza*), representing a marked deviation from the alloys employed in earlier Portuguese foundries. These values considerably exceed the 15% threshold, above which the risk of dezincification increases, a process involving the selective removal of zinc from the alloy, resulting in a porous matrix of copper and copper oxides with significantly diminished mechanical strength (Canadian

Conservation Institute, 2015; Copper Development Association Inc., n.d.; Davis, 2001). Although no visible signs of this phenomenon were observed in the sculptures, their composition renders them potentially vulnerable to this type of long-term deterioration.

In contrast, *O Trabalho*, cast only two years later, exhibits lower zinc levels (ranging from 5.9% to 11.3%) and a formulation more in line with recipes used in previous decades. This difference may indicate an evolution in the bronze formulations employed by the foundry throughout the 1950s, possibly adapted to the specific characteristics of each commission and the availability of alloying elements.

Finally, the sculpture *Figura Feminina*, cast in 1965 by commission of the ESBAP and also produced at the José Castro Guedes foundry, presents a formulation similar to *O Trabalho*, with high copper content (between 86.6% and 89.6%) and moderate zinc levels (between 5.3% and 8.9%). Tin, by contrast, appears in very low concentrations (around 1%), which may reflect an cost optimisation of materials, given the significantly lower abundance of tin in the earth crust compared to zinc (Venditti & Le Pan, 2021).

Analytical Overview of the Evolution of Bronze Alloys in Sculpture (1885–1965)

During the 19th century, a variety of bronze formulations were employed in sculpture, without a clear predominance of binary alloys. Although the bust of Francisco de Almada e Mendonça exhibits an exceptionally high tin content and no detectable zinc or lead, the few other examples analysed from that period or earlier show a tendency towards copper–tin–zinc–lead compositions. The equestrian statue of King José I (1775), for instance, was cast using a bronze rich in zinc (Salta & Fontinha, 1998b), while the statue of King Pedro IV, cast in Belgium in 1866, also presents a quaternary formulation more in line with Portuguese 20th-century sculptures (R. Fontinha & Salta, 1996b). In this context, the *Almada e Mendonça* bust appears to be an exception and cannot be considered representative of broader alloying practices. The statue of King Afonso Henriques, cast in Porto in 1887, also employed a copper–tin–zinc–lead alloy, confirming the predominance of this formulation in

Portuguese sculpture. Indeed, among Portuguese sculptures whose compositions have been studied, only the statue of the *Marquês de Pombal*, cast in 1934 (Salta & Fontinha, 1998a), presents a binary copper-tin alloy, reinforcing the idea that such formulations were exceptions rather than the rule within the national sculptural repertoire.

From the 1920s onwards, a trend towards more homogeneous quaternary alloys can be observed, with lower tin contents (2%–5%) and the systematic presence of zinc (5%–9%) and lead (up to 1.6%). This pattern is consistent in sculptures such as *S. José*, *S. Joaquim*, *O Pescador*, and *Academia – Homem Sentado*, and seems to reflect a degree of standardisation in bronze formulations used by industrial foundries such as Adelino Sá Lemos, linked to institutional commissions. The bust of João Marques de Oliveira, cast in Paris by the Hébrard foundry, stands out as an exception within this group, with a notably higher tin content and more complex composition, suggesting a more refined technical approach tailored to a more demanding artistic market.

Among sculptures cast between 1940 and 1965, the compositions diversify further. Some works, such as *O Trabalho* or *Figura Feminina*, retain alloy profiles similar to those of the 1920s, with balanced levels of tin, zinc and lead. In contrast, sculptures such as *A Música* and *A Riqueza* introduce particularly high zinc contents (above 30% and 16%, respectively), which, while enhancing certain casting properties, may increase susceptibility to degradation phenomena such as dezincification. The case of the bust of *Francisco Pinto Bessa*, with 8% lead in one area, illustrates a specific adjustment of the formulation to improve fluidity, a rather uncommon approach in lost-wax casting, where such modifications are usually unnecessary.

This evolution in alloy composition is also evident in quantitative terms. Figure 5.38 presents the average percentage of the main alloying elements, excluding copper, found in the sculptures analysed, grouped by decade between 1885 and 1965. This graphical approach enables a clearer visualisation of general compositional trends in bronze sculpture over time, including the progressive incorporation of zinc and lead, as well as the decreasing average tin content in certain phases.

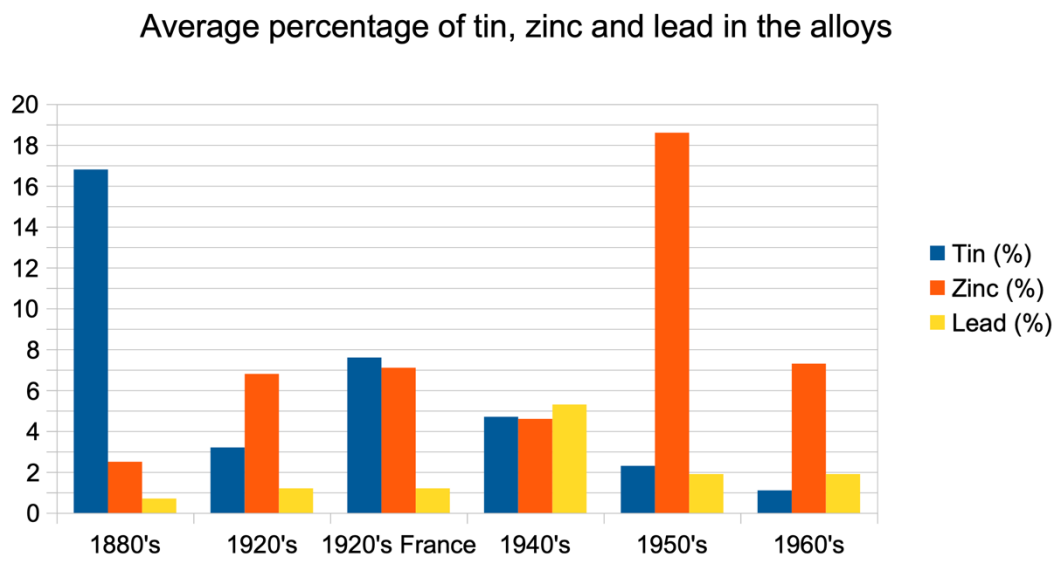


Fig. 5.38 - Average percentage of the main alloying elements (Sn, Zn, Pb) identified in the sculptures analysed, cast between 1880 and 1965. Copper is excluded to better highlight trends in secondary elements. Data is grouped by decade. Results from welding areas on the sword of King Afonso Henriques were omitted to reflect only original casting composition. The bust of Marques de Oliveira, cast in France, is presented separately. Data compiled from EDXRF analysis. Average copper contents per group: 1880s – 78.5%, 1920s – 87.4%, 1920s (France) – 79.8%, 1940s – 84.5%, 1950s – 76.2%, 1960s – 88.4%.

Overall, the results point to a significant evolution in the formulation of sculptural alloys between 1885 and 1965. While some pieces exhibit specific variations attributable to later interventions, functional requirements, or particular construction techniques, general trends are discernible. These include a relative compositional uniformity in works from the 1920s and a gradual increase in zinc levels in sculptures from the 1950s onwards. This evolution appears to reflect technical factors, such as changes in casting practices, the availability of raw materials, and a progressive standardisation in alloy recipes.

In compositional terms, the analysed sculptures exhibit a high proportion of copper, typically above 70%, and exceeding 80% in most 20th-century works. These levels are consistent with findings from other studies on bronze alloys used in 19th- and 20th-century cast sculpture (Neiva et al., 2008; Pouyet et al., 2019; L. S. Selwyn et al., 1996; M. L. Young & Dunand,

2015), reinforcing the validity of this study's results within a broader technical and historical framework.

As discussed in Chapter 1, it was common practice in Portuguese foundries to acquire metals separately or in the form of scrap, rather than purchasing pre-alloyed bronze. According to Carlos Bernardino, this approach, combined with the absence of equipment for precise component quantification, force foundrymen to assess the quality of the alloy through empirical methods (C. Bernardino, personal communication, February 2021). Moreover, the exact composition of acquired metals could not always be verified, increasing the likelihood of incorporating unexpected elements in the final alloy. This structural condition of local production may account for part of the compositional variability observed, even among sculptures produced in similar contexts and periods.

5.4.2 Analysis of corrosion

XRD analysis carried out on the sculptures under study has revealed a notable variety of corrosion products, reflecting not only the original alloy compositions but also the environmental conditions, exposure contexts and, in some cases, previous conservation treatments.

In sculptures located outdoors in the city of Porto, such as the busts of *Francisco de Almada e Mendonça* and *João Marques de Oliveira*, as well as *Figura Feminina*, a recurring combination of products has been identified, including cuprite, brochantite, atacamite and, in some cases, silicon oxides and phosphates. The frequent occurrence of atacamite, a basic copper chloride, suggests prolonged exposure to saline influence, likely related to the city's proximity to the sea and high ambient humidity (Knotkova & Kreislova, 2007; Krätschmer et al., 2002). In certain cases, such as the bust of João Marques de Oliveira, more complex compounds such as cobalt-copper-tin were also identified, possibly linked to specific materials applied during a vandalism-related intervention.

The simultaneous presence of brochantite and antlerite on the bust of *Francisco de Almada e Mendonça* reflects fluctuating atmospheric conditions throughout its exposure. Both minerals are commonly found in patinas formed on copper alloys exposed to urban and industrial environments (Schlesinger et al., 2000; Scott, 2002). These patinas are characterised by their bluish-green colour, attributable to the presence of copper (II) ions in the outer corrosion layer (Leygraf et al., 2019).

The statue of *King Afonso Henriques*, located in Guimarães, presents a different scenario. Although the city is distant from marine environments and industrial activity is limited, corrosion products such as cuprite, brochantite, posnjakite and cassiterite were identified. Posnjakite is associated with low-sulphur environments (Zittlau et al., 2013), in alignment with the local atmospheric conditions. Cassiterite (SnO_2), in turn, indicates advanced alteration of the tin in the original alloy, formed by the dissolution and oxidation of tin, suggesting a prolonged or locally intensified degradation process (Bernard & Joiret, 2009). In some samples, quartz was also detected, probably due to the deposition of airborne particles. In the sword area specifically, compounds such as tenorite (CuO) were also found, likely formed on the exposed metal surface under microclimatic stress.

Beyond the XRD results, SEM-EDS analysis of a metallic fragment extracted during the cleaning intervention provided additional insight into corrosion processes affecting the statue of *King Afonso Henriques*. Line-scan analysis revealed a gradual depletion of copper towards the surface, while tin showed a marked increase in that direction, suggesting selective corrosion processes compatible with the formation of tin oxides such as cassiterite (SnO_2). These results supplement the data obtained by XRD, offering a more nuanced view of the chemical evolution of the alloy as it transitions towards the patina.

An unusual feature observed in this sculpture was the detection of a copper–tin phase tentatively identified as $Sn_{11}Cu_{40.5}$ in samples from both the front and back of the statue. Given the limitations of XRD in distinguishing between closely related Cu–Sn phases, this result should be interpreted with caution and may correspond either to remnants of the

original alloy microstructure or to ambiguities in phase identification due to overlapping diffraction peaks or incomplete reference databases in the XRD analysis.

The sculptures currently housed at the MNSR, *S. José* and *S. Joaquim*, display corrosion processes developed during their long-term residence in indoor museum conditions. Although the general environment is relatively stable, localised alterations have been identified, mainly in areas of dust accumulation, which can lead to microenvironments with retained moisture and pollutants, thereby promoting corrosion (Couture-Rigert et al., 2012; Podany, 2006). In *S. José*, brochantite was identified, pointing to slow sulphation processes driven by ambient humidity and the deposition of atmospheric contaminants.

In contrast, *S. Joaquim* showed the presence of both posnjakite and atacamite, products that also form under high humidity, though they differ chemically: posnjakite is a hydrated sulphate, while atacamite is a basic copper chloride. In both cases, these corrosion products were found in specific green areas on the surface**,** in stark contrast to the intact brown artificial patina still covering most of the sculptures.

Furthermore, in *S. Joaquim*, paraffin wax, silicon phosphate, and barium chloride hydrate were identified, compounds possibly related to past conservation treatments. Paraffin has historically been used in metal conservation as a protective coating due to its hydrophobic nature and its ability to form a physical barrier against moisture and other atmospheric agents.

A comparative assessment of these results highlights that outdoor sculptures present a greater diversity of corrosion products, including both chlorinated and sulphated phases, whereas those housed in the museum environment display a more limited set of products, likely linked to slower and more localised alteration processes. Table 5.24 summarises the presence of corrosion compounds identified by XRD across the studied sculptures. The objects are grouped according to their conservation context: urban outdoor exposure (Porto), inland outdoor exposure (Guimarães), and a controlled indoor museum setting (MNSR). This classification facilitates the observation of compositional patterns related to

environmental conditions, such as temperature, humidity, atmospheric pollutants and previous conservation interventions.

Table 5.24 Presence of corrosion products identified by XRD in the sculptures studied, organised according to conservation environment. The main crystalline phases are listed along with other compounds associated with previous treatments or environmental contamination.

Sculpture	F. de Almada e Mendonça	K. Afonso Henriques	K. Afonso Henriques (sword)	S. José	S. Joaquim	M. de Oliveira	Figura Feminina
Setting	Outdoor (Porto)	Outdoor (Guimarães)	Outdoor (Guimarães)	Indoor (MNSR)	Indoor (MNSR)	Outdoor (Porto)	Outdoor (Porto)
Cuprite		**X**	**X**	**X**	**X**	**X**	**X**
Tenorite			**X**				
Cassiterite		**X**					
Posnjakite		**X**	**X**		**X**		
Brochantite	**X**	**X**	**X**	**X**			
Antlerite	**X**						
Atacamite	**X**				**X**		**X**
Quartz		**X**	**X**	**X**			
Other coatings, dust, etc.	Magnesium sulphite hydrate	Copper- tin					

A detailed analysis of the corrosion products offers not only an assessment of the sculptures' current condition, but also provides a solid foundation for evaluating their long-term behaviour in response to different environmental contexts. This aspect will be further explored in subsequent chapters, where conservation strategies and risk assessments specific to each sculpture will be discussed.

5.5 FINAL REMARKS ON CHAPTER 5

The comprehensive study of sculptural alloys and their corrosion products has enabled the identification of significant patterns in the technical and material practices of Portuguese public sculpture between 1885 and 1965. Many of the sculptures analysed feature quaternary copper-based alloys containing tin, zinc, and lead, employed with relative consistency throughout the period. Only in isolated cases, such as the bust of *Francisco de Almada e Mendonça*, was a binary formulation identified, whose exceptional nature suggests that this alloy type did not constitute a predominant practice, at least among the Portuguese sculptures whose composition has been studied to date.

The results obtained through non-destructive techniques (EDXRF), complemented by XRD and optical microscopy and SEM-EDS analyses in selected cases, have demonstrated the value of a multi-technique approach in characterising both the original alloy composition and the alteration processes affecting the sculptures over time. In particular, the investigations carried out on the statue of *King Afonso Henriques* allowed for the observation of selective corrosion phenomena, differential elemental distribution, indicating the complexity of the alloy microstructure and its alteration during corrosion processes

Moreover, the identification of corrosion products such as brochantite, atacamite, and cassiterite demonstrate a strong correlation between alloy composition, the material

condition of the sculpture, and the environment in which it has been exposed. While outdoor sculptures exhibit a broader diversity of sulphated and chlorinated phases, those preserved in museum environments display more localised transformations, often associated with dust accumulation and residual humidity. The occurrence of chloride-based products such as atacamite in one museum-held sculpture underscores how microclimatic factors, including retained moisture and airborne contaminants, can contribute to the formation of such compounds even in seemingly stable indoor settings.

Taken together, this chapter provides a foundation for understanding the technological evolution of copper-alloy sculpture in Portugal, as well as the material and environmental factors that have shaped their present state of conservation. This knowledge is essential not only for the historical and technical interpretation of these works, but also for the development of more informed and sustainable conservation strategies.

CHAPTER 6. CORROSIVE ENVIRONMENTS AND THEIR IMPACT ON SOARES DOS REIS' SCULPTURES: A SCIENTIFIC REVIEW AND CASE STUDY APPROACH

This chapter examines the environmental conditions that influence the deterioration of copper alloy sculptures, with a particular focus on the works of Soares dos Reis. Engaging critically with the scientific literature, it analyses how variables such as air pollutants, humidity, temperature fluctuations and volatile organic compounds shape corrosion processes in both outdoor and indoor settings, and how these patterns relate to the case studies introduced in Chapter 5.

Understanding these environmental influences is fundamental to diagnosing the chemical and physical alterations observed in bronze surfaces, including the formation of reactive corrosion products, changes in patina morphology and the disruption of protective layers. These manifestations are not only symptomatic of broader environmental dynamics but also decisive for determining the urgency and nature of conservation responses.

The aim is to establish a theoretical and comparative framework that supports the interpretation of deterioration processes and informs conservation strategies tailored to the specific microclimatic and atmospheric conditions affecting each object.

6.1 CORROSION PROCESSES IN COPPER ALLOYS: SCIENTIFIC BACKGROUND

6.1.1 Environmental Factors in Outdoor Corrosion of Copper Alloys

The corrosion of copper alloy sculptures is strongly influenced by environmental agents such as air pollutants, humidity, and temperature fluctuations. This section draws on key scientific studies that explore how these variables affect corrosion dynamics in both outdoor and indoor settings, with particular attention to conditions similar to those in the case studies. The aim is to outline the principal environmental drivers identified in published research and to examine how they interact with the physical and chemical characteristics of copper alloy surfaces.

Various authors have noted that location, microclimate, and air composition are determining factors in the types of corrosion processes that manifest in metal artworks. In urban or industrial environments, pollutants such as sulphur dioxide (SO_2), nitrogen oxides (NO_x), chloride compounds (Cl^-), and ozone (O_3) have been shown to accelerate the formation of active corrosion products, resulting in structural alterations to the metallic substrate (Knotkova & Kreislova, 2007; Krätschmer et al., 2002; Robbiola et al., 1998). In contrast, in atmospherically low-aggressiveness settings, such as controlled museum interiors or rural areas, oxidation processes tend to form more stable films, commonly referred to as patinas, which may act as protective layers (Bernardi, Chiavari, et al., 2009; Chiavari et al., 2007; Dermaj et al., 2007; Knotkova & Kreislova, 2007; Mazzeo, 2004; Mills, 1990).

From a comparative perspective, the specialised literature classifies corrosion processes into two main categories: *benign corrosion* and *malignant corrosion*. The former is linked to the formation of stable, low-solubility and adherent alteration products, such as certain natural patinas, which act as passive barriers and provide a degree of protection against further environmental exposure. In contrast, malignant corrosion is associated with the formation of

unstable and highly reactive compounds, such as certain sulphates and chlorides, which result from the interaction between the metal alloy and atmospheric pollutants under conditions of high relative humidity (RH) or temperature. These compounds not only lack protective capacity, but also tend to retain moisture, reactivating corrosion processes and accelerating the deeper degradation of the metal.

The effects of marine aerosols also play a significant role in the corrosion of outdoor copper alloy sculptures. Studies conducted in coastal environments have demonstrated the influence of chloride ions on the formation of complex corrosion layers, often characterised by porous structures and the presence of copper chlorides, such as nantokite and atacamite, which are known to promote active corrosion cycles (Chang et al., 2020; Gianni, 2011; Knotkova & Kreislova, 2007; Krätschmer et al., 2002; Veleva & Farro, 2012; X. Zhang et al., 2014).

Temperature and RH are additional factors that modulate the aggressiveness of the environment. High humidity levels, especially in combination with air pollutants, can increase the conductivity of surface films, enabling electrochemical reactions that facilitate corrosion (N. Baer, 1988; Chiavari et al., 2006; Strandberg, 1997). Furthermore, daily and seasonal fluctuations in temperature and moisture may contribute to the expansion and contraction of corrosion products, generating mechanical stress on the metal surface. In this context, wet-dry cycles to which many copper alloy sculptures are exposed, particularly in outdoor settings, promote the dissolution and recrystallisation of soluble compounds, such as chlorides and certain sulphates, thereby increasing surface reactivity and accelerating degradation processes (EL-Mahdy, 2005; Gianni, Cavallini, Natali, et al., 2013; Kong et al., 2016).

Indoor environments are not exempt from these processes, particularly in historic buildings with inadequate environmental control. Copper alloy objects displayed indoors may be affected by volatile organic compounds (VOCs), such as acetic acid (CH_3COOH), formic acid (CH_2O_2) and formaldehyde (CH_2O), which are emitted from wooden furniture, pressed wood products, display cases, conservation materials, treated textiles and construction elements such as varnishes, adhesives and resins. These compounds have been identified as

corrosive agents capable of producing localised and often irregular corrosion patterns, especially within confined microclimates (Caple, 2012; Lafuente et al., 2013; López-Delgado et al., 2001). The growing trend towards reconfiguring exhibition spaces for each installation has raised increasing concern regarding the presence of these acids, as the materials used are rarely subjected to compatibility testing prior to use (Lafuente et al., 2013).

In addition to atmospheric agents and volatile organic pollutants, certain biological or anthropogenic factors may also induce corrosion in copper alloy sculptures. A recurring example in outdoor sculptures is the impact of bird droppings, particularly from pigeons, which contain uric and phosphoric acids capable of generating localised and accelerated corrosion on exposed metal surfaces (Balogh, 2017; Bernardi, Bowden, et al., 2009; Vasiliu & Buruiana, 2010). Similarly, direct handling of the sculptures, whether by the public or during maintenance activities, can leave behind greasy residues or contaminants that alter the surface chemistry and promote corrosive processes. Human sweat predominantly contains chloride, sodium and potassium ions, along with urea, lactic acid, and traces of nitrates, phosphates and sulphates, all of which are potentially corrosive upon prolonged contact with metal alloys (Fredj et al., 2013; Hostýnek, 2004; Lind, 1972).

6.1.2 Formation and structure of patina in copper alloys

Depending on the pollutants present in the environment, surfaces of copper and its alloys may develop patinas composed of two to four layers. These layers, primarily formed by copper oxides, are relatively chemically homogeneous, and present irregular crystalline formations (Graedel et al., 1987; Knotkova & Kreislova, 2007; Šatović et al., 2009).

Robbiola et al. (1998) proposed a classification system for patinas developed on copper alloys in archaeological contexts, distinguishing between two main types. Type I consists of two layers formed through a natural and gradual interaction between the metal and its

environment, leading to surface decuprification and the development of a stable greenish-blue film that acts as a passive barrier. In contrast, Type II comprises more complex patinas made up of three or more layers, formed under more aggressive environmental conditions. These tend to exhibit rougher surfaces and a high concentration of chlorides, which can induce localised corrosion such as pitting.

Although this classification was originally developed in the field of archaeometallurgy, it is equally relevant to the study of exposed copper alloy sculptures. The distinction between protective and active or unstable layers offers valuable insight into the behaviour of corrosion products, depending on the aggressiveness of the surrounding environment and the interaction between the alloy and atmospheric pollutants.

Type I, First Layer: Initial Oxidation

In the early stages of corrosion, copper alloys undergo an oxidation rate similar to that of pure copper, estimated at approximately 0.1 mpy (mils per year) (Schumacher, 1979, as cited in Hutchison & Scully, 2018). As a result, the first layer of the patina forms, composed predominantly of copper oxides. This layer displays colours ranging from deep red to brown and is characterised by its semiconducting properties (Leygraf et al., 2019).

The layer mainly consists of copper (I) and (II) oxides, namely cuprite[61] (Cu_2O) and tenorite[62] (CuO), respectively. Cuprite, with its reddish tone, and tenorite, which is dark brown or black, are corrosion products that form during the initial phases of degradation in copper and its alloys. Both compounds adhere strongly to the metallic surface, functioning as primary oxidation products that may vary in thickness and contribute to the long-term consolidation of the patina (Bernard & Joiret, 2009; Knotkova & Kreislova, 2007; Krätschmer et al., 2002; Marušić et al., 2009; Šatović et al., 2013; Scott, 1997; L. S. Selwyn et al., 1996).

This first layer develops progressively and may reach several micrometres in thickness after years of exposure. In outdoor environments, cuprite has been identified as the dominant mineral on the surface of the metal, while tenorite tends to occur less frequently (Scott, 2002). In sculptures exposed over long periods, cuprite may account for up to half of the total mass of the patina. This layer continues to evolve over time, reaching thicknesses in the order of tenths of a micrometre (Hemming, 1977; Krätschmer et al., 2002). From a

[61] Cuprite is a copper (I) oxide with an isometric crystal structure, known for its broad chromatic range, which extends from ruby red or cochineal red to nearly black tones, occasionally exhibiting bluish or yellowish hues. It typically occurs as a transparent to translucent mineral, with an adamantine, submetallic, or occasionally earthy lustre. The name *cuprite* was proposed by Wilhelm Karl von Haidinger, in reference to the Latin term *cuprum*, alluding to its copper-based composition. It is a widely distributed mineral species found throughout the world, commonly associated with other copper-bearing minerals such as native copper, tenorite, malachite, azurite, calcite, brochantite, antlerite, atacamite, and chrysocolla. It may also occur in association with iron oxides and clay minerals (Hudson Institute of Mineralogy, 2021; Mineralogical Society of America, 2005).

[62] Tenorite, also known as melaconite, is a copper (II) oxide with a monoclinic crystal structure, characterised by its dark grey to matte black colour and distinctive metallic lustre. It was first identified in 1841 in the vicinity of Mount Vesuvius by Michele Tenore (1780–1861), a botanist and professor at the University of Naples, after whom the mineral is named. This mineral has a Mohs hardness of 3 to 4 and a density ranging from 5.8 to 6.4 g/cm^3. It is a widely distributed mineral species found globally, commonly associated with other copper minerals such as cuprite, chrysocolla, malachite, and azurite. It may also occur in association with mixed iron-manganese (Fe-Mn) oxides, copper chlorides, alkali chlorides, and cotunnite (Anthony et al., 2003b; Torres, n.d.).

structural perspective, it tends to form a dense, continuous film that adheres well to the metallic core. However, its stability may be compromised by the presence of soluble salts, thermal stress, or mechanical action, all of which can promote the appearance of microcracks and fissures in the oxidised surface (Matteini et al., 2016; Strandberg, 1997).

In copper alloys that contain tin as part of their composition, this element can oxidise and lead to the formation of cassiterite[63] (SnO_2), which is the mineral form of tin (IV) oxide (Bernard & Joiret, 2009). This corrosion product generally forms between the metallic surface and the corrosion layer composed of copper oxides such as cuprite and tenorite (Šatović et al., 2013). Cassiterite is a highly stable mineral under most environmental conditions, and its presence in the patina has been associated with enhanced protective properties of the surface. It acts as an effective passive layer by reducing the corrosion rate of the underlying cuprite (Chase et al., 2007; Gianni, Cavallini, & Adriaens, 2013; Zhou & Ogle, 2018). The layer formed by the aforementioned tin and copper oxides can range in thickness from 10 to 250 μm, depending on the environmental conditions and the specific composition of the alloy (Robbiola et al., 1998).

The presence of cassiterite in the passive patina highlights the crucial role of tin in the corrosion resistance of copper alloy. Several studies have shown that a higher proportion of tin in the alloy's composition increases its protective capacity against moderately aggressive corrosive agents, even on surfaces without additional coatings or artificial patinas (Chiavari et al., 2007; Muller et al., 2010, 2013; Robbiola et al., 1998; Robbiola, Fiaud, & Harch, 1993; Šatović et al., 2009). However, the role of tin is not exclusively inhibitory: during

[63] Cassiterite is a tin oxide mineral (SnO_2) that can occur in nature in a wide chromatic range, including black, yellow, brown, reddish, or white tones. It is characterised by a lustre that varies from adamantine to greasy and submetallic, as well as by its high density and intense brilliance on fresh surfaces. It is the principal ore of tin worldwide and is typically found in high-temperature hydrothermal veins and in pegmatites, often associated with granitic intrusions. Cassiterite has a Mohs hardness of 6 to 7, which gives it notable mechanical resistance (Mindat.org & Hudson Institute of Mineralogy, 2022).

certain corrosion processes, it may act as a contributing factor in accelerating copper dissolution, depending on the electrochemical conditions of the environment (Zhou & Ogle, 2018).

Type I, Second Layer: Formation of Basic Copper Sulphates

In atmospheres containing sulphur compounds, particularly sulphur dioxide (SO_2), the formation of the second layer of the patina on copper alloys is driven by the interaction of these agents with the oxidation products present in the first layer, mainly cuprite (Cu_2O) and tenorite (CuO). These pollutants react with the copper oxides, resulting in the precipitation of basic copper sulphates, which are deposited in solid form on the underlying layer (Knotkova & Kreislova, 2007). The specific mineralogical composition of this second layer depends on several factors, including the atmospheric concentration of sulphur compounds, environmental pH, temperature, and, in particular, RH.

The rate of formation of these compounds is especially influenced by RH, with a marked acceleration when values fall between 63% and 75%, a critical range that promotes the dissolution of hygroscopic salts and the mobility of ions on the metal surface (Vernon, 1931). Furthermore, the type of sulphate that crystallises depends on the thermodynamic balance among these parameters, leading to the development of different mineral phases depending on the local environmental conditions.

Under conditions of low atmospheric sulphur pollution, the second layer may begin with the precipitation of posnjakite[64] ($Cu_4(SO_4)(OH)_6 \cdot H_2O$), a hydrated basic sulphate that forms at

[64] Posnjakite is a basic hydrated copper sulphate, with the chemical formula $Cu_4(SO_4)(OH)_6 \cdot H_2O$, which crystallises in the monoclinic system. It typically occurs as sky-blue crusts or aggregates, with a vitreous lustre and a Mohs hardness of 2.5 to 3. It is a secondary mineral, commonly found in the oxidation zones of copper deposits, where it is associated with brochantite, langite, azurite, or malachite. It was first described in 1967

moderate temperatures, between 20 °C and 40 °C (Zittlau et al., 2013). Over time, and as a result of rising temperatures or changes in pH, this mineral can gradually transform into brochantite[65] ($Cu_4SO_4(OH)_6$), a more stable compound that crystallises between 40 °C and 50 °C and remains in equilibrium up to 85 °C, provided the pH remains close to 7.5 (Zittlau et al., 2013). Brochantite is one of the most commonly identified minerals in patinas formed in urban and industrial environments (Bureš et al., 2019; Krätschmer et al., 2002; Lago et al., 2002).

In atmospheres with higher concentrations of sulphur compounds or more acidic pH, minerals such as strandbergite[66] ($Cu_{2.5}(SO_4)(OH)_3 \cdot 2H_2O$) may form, acting as a precursor to antlerite[67] ($Cu_3(SO_4)(OH)_4$), a more stable and thermodynamically favoured corrosion

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and named in honour of the geochemist Eugene V. Posnjak (Hudson Institute of Mineralogy, n.dc; RRUFF Project, n.d).

[65] Brochantite is a copper hydroxysulphate with the formula $Cu_4(SO_4)(OH)_6$, crystallising in the monoclinic system. It occurs as acicular crystals or fibrous aggregates in emerald to dark green colours, with a vitreous to pearly lustre. It has a Mohs hardness of 3.5 to 4 and a specific gravity of approximately 3.9 g/cm³. It is a secondary mineral, typically found in oxidised zones of copper deposits, where it is associated with malachite, azurite, chrysocolla, and cuprite. It was described in 1824 and named after André J. F. M. Brochant de Villiers (Hudson Institute of Mineralogy, n.da; Museum of Fine Arts, Boston, n.db).

[66] Strandbergite, also known as Kobyashevite when found in natural settings, is a hydrated copper hydroxysulphate with the chemical formula $Cu_{2.5}(SO_4)(OH)_3 \cdot 2H_2O$, crystallising in the triclinic system. It occurs as a secondary phase with a bluish-green to dark green colour, vitreous lustre, and an approximate Mohs hardness of 2.5. This mineral is characteristic of historical patinas formed in environments with high levels of sulphur dioxide, where it may act as a precursor to more stable phases such as antlerite (Krätschmer et al., 2002; Hudson Institute of Mineralogy, n.db; Mineralienatlas Team, n.d).

[67] Antlerite is a copper hydroxysulphate with the formula $Cu_3(SO_4)(OH)_4$, crystallising in the orthorhombic system. It occurs as a secondary phase with emerald to dark green colour, vitreous lustre, and a Mohs hardness of 3 to 3.5. It typically forms in the oxidised zones of copper deposits under arid and acidic conditions and is commonly found in historical patinas on copper alloy exposed to sulphur dioxide-rich atmospheres (Hudson Institute of Mineralogy, n.da; Museum of Fine Arts, Boston, n.d.; RRUFF Project, n.da).

product (Bureš et al., 2019; Krätschmer et al., 2002). Both brochantite and antlerite are characterised by their bluish-green colour, resulting from the presence of copper (II) ions, and are frequently found in urban environments with acidic and humid atmospheric conditions (Leygraf et al., 2019; Schlesinger et al., 2000; Scott, 2002).

The formation of these minerals is closely linked to the level of environmental acidity: while brochantite may develop under slightly acidic or neutral conditions, antlerite requires a clearly lower pH to crystallise. This has led some authors to consider its presence a possible indicator of strongly acidic environments, although this interpretation remains a subject of debate (Castro et al., 2008; Lago et al., 2002; Scott, 2002).

Type II: Complex Corrosion Products in Aggressive Environments

In marine contexts or areas with high environmental salinity, such as natural salt flats, coastal regions, or industrial environments with saline aerosols, the outer layers may be dominated by the presence of copper chlorides, such as atacamite[68] ($Cu_2Cl(OH)_3$) and paratacamite[69] ($(Cu^{2+})_3(Cu,Zn)(OH)_6Cl_2$) (Knotkova & Kreislova, 2007; Krätschmer et al., 2002). These

[68] Atacamite is a copper hydroxychloride with the formula $Cu_2Cl(OH)_3$, crystallising in the orthorhombic system. It occurs as prismatic or acicular crystals with an emerald to dark green colour, vitreous to adamantine lustre, and a Mohs hardness of 3 to 3.5. This secondary mineral typically forms in the oxidised zones of copper deposits in arid climates and is commonly found in historical patinas on copper alloy exposed to chloride-rich environments (Hudson Institute of Mineralogy, n.d.; Museum of Fine Arts, Boston, n.da; RRUFF Project, n.da).

[69] Paratacamite is a copper hydroxychloride with the formula $Cu_3(Cu,Zn)(OH)_6Cl_2$, crystallising in the trigonal system. It forms as rhombohedral crystals of dark green to greenish-black colour, with a vitreous lustre and a Mohs hardness of 3. It is a secondary mineral, polymorphous with atacamite, clinoatacamite, and botallackite, typically occurring in arid or saline environments within the oxidation zones of copper deposits (Hudson Institute of Mineralogy, n.d.; RRUFF Project, n.d.).

bluish-green minerals form through the combined action of chloride ions and moisture on the underlying copper oxide layers. Unlike basic sulphates, chloride-based corrosion products tend to crystallise in less stable forms, producing porous structures that retain moisture and reactivate corrosion processes, particularly in wet-dry cycles.

In subterranean environments or those associated with burial contexts, the most commonly encountered corrosion product is malachite[70] ($Cu_2CO_3(OH)_2$), a basic copper carbonate that forms in the presence of carbon dioxide and moisture. While typically associated with archaeological objects, it may also appear on works exposed to specific urban microclimates or in contact with carbonate-based materials (Gianni, 2011; Scott et al., 1994).

In environments with nitrogen-containing compounds, gerhardtite[71] ($Cu_2(NO_3)(OH)_3$) can develop, although its presence in copper alloys is rare (Knotkova & Kreislova, 2007; Scott, 2002). This green copper hydroxynitrate has been identified on sculptures exposed to urban atmospheres, where its occurrence may be linked to contaminated microclimates and localised nitrate accumulation. A related compound, rouaite[72] ($Cu_2(NO_3)(OH)_3$), has also

[70] Malachite is a basic copper carbonate with the formula $Cu_2CO_3(OH)_2$, crystallising in the monoclinic system. It typically forms as botryoidal, stalactitical or fibrous aggregates with a vivid to dark green colour, vitreous to silky lustre, and a Mohs hardness of 3.5 to 4. It is a secondary mineral, commonly found in the oxidation zones of copper deposits, and frequently associated with azurite, cuprite and calcite (Anthony et al., 2003; Hudson Institute of Mineralogy, n.db; RRUFF Project, n.da).

[71] Gerhardtite is a basic copper nitrate with the formula $Cu_2(NO_3)(OH)_3$, crystallising in the orthorhombic system. It occurs as tabular crystals or massive aggregates with a vivid green to bluish-green colour, vitreous lustre, and a Mohs hardness of 2. This rare secondary mineral forms in the oxidised zones of copper deposits and is commonly associated with minerals such as cuprite, malachite, atacamite, and brochantite. It is dimorphous with rouaite (Anthony et al., 2003; Hudson Institute of Mineralogy, n.d.; RRUFF Project, n.d.).

[72] Rouaite is a rare secondary mineral classified as a basic copper nitrate, with the chemical formula $Cu_2(NO_3)(OH)_3$. It appears as bluish or greenish-blue crystals and typically forms in highly oxidising environments rich in nitrates. Its presence may indicate advanced stages of alteration on copper alloys, particularly in archaeological contexts or in areas exposed to nitrogen-based pollutants (Hudson Institute of Mineralogy, n.d.d).

been observed; this is a less stable polymorph with similar characteristics that forms at temperatures above 140 °C (Couture-Rigert et al., 2012).

Across these successive layers, several studies have also identified the presence of siliceous impurities, such as quartz, calcium, and airborne dust particles, that become incorporated during the formation of the corrosion layer (Boccaccini et al., 2023; Ghoniem, 2011). These inclusions can increase the thickness of the structure, alter its morphology, and reduce the adhesion of the corrosion layer to the metal. Moreover, the porous configuration of the outer layers, combined with the existence of microcavities, facilitates the movement of ions between strata, thereby intensifying the dissolution and recrystallisation processes that characterise metal surfaces in polluted environments (Knotkova & Kreislova, 2007).

In summary, the formation and structure of corrosion on copper alloys result from a complex interaction between the properties of the metal and the environmental conditions. While Type I corrosion tends to be stable and protective, Type II reflects more aggressive corrosive processes, driven by specific pollutants and harsh environmental factors. This distinction not only aids in interpreting the surface evolution of copper alloy sculptures, but also supports the material diagnosis. In this context, the typology proposed by Robbiola et al. (1998) emerges as a key tool for understanding the degradation of metal surfaces and informing conservation strategies.

6.1.3 Environmental Conditions and Corrosion in Indoor and Museographic Settings

Although the atmospheric aggressiveness in indoor spaces is generally lower than in outdoor environments, various studies have demonstrated that certain specific conditions can induce significant corrosion processes in bronze objects, particularly in museographic contexts or historic buildings adapted for exhibition use. Air quality, RH, limited ventilation, and the presence of building materials that emit corrosive compounds directly influence the

formation and progression of corrosion products on metallic surfaces (Bartuli et al., 1999; Šatović et al., 2013; Graedel, 1987, apud Strandberg, 1997).

In particular, the emission of volatile organic compounds, such as acetic acid[73] (CH_3COOH), formic acid[74] (CH_2O_2), and formaldehyde[75] (CH_2O), has been documented from sources including wood, varnishes, adhesives, paints, resins and other materials commonly used in display cases, exhibition furniture or mounting systems (Caple, 2012; Lafuente et al., 2013; López-Delgado et al., 2001). These agents, even at low concentrations, have been associated with the formation of irregular patinas and the appearance of secondary corrosion compounds with potentially damaging effects.

[73] Acetic acid is a short-chain carboxylic acid, colourless, volatile, and with a pungent odour, widely recognised as the main component of vinegar in its diluted form. In museographic contexts, it is released as a volatile organic compound from wood, varnishes, adhesives, and other organic materials used in furniture or display cases. With a boiling point of 118 °C and high solubility in water, it can react with metal surfaces, particularly copper alloys, forming corrosion products such as copper(II) acetate, which contribute to the deterioration of heritage metals in enclosed environments (Caple, 2000; Lafuente et al., 2013; Museum of Fine Arts, Boston, n.da).

[74] Formic acid is the simplest carboxylic acid, organic in nature, colourless, volatile, and characterised by a sharp odour. Although it occurs naturally in some biological processes, within museographic environments it is primarily released by wood, adhesives, varnishes, and other construction or display materials. It has a low boiling point (100.8 °C) and is soluble in water and most organic solvents. In enclosed spaces, its presence can lead to localised corrosion on metals such as copper, generating unstable alteration products that compromise the integrity of heritage surfaces (Caple, 2000; Lafuente et al., 2013; Museum of Fine Arts, Boston, n.db).

[75] Formaldehyde is a colourless volatile organic compound with a pungent and irritating odour, and the chemical formula CH_2O. It is widely used in the chemical and manufacturing industries, as well as in consumer products such as particleboard, adhesives, and textiles. It is recognised as a human carcinogen and may cause adverse health effects, particularly in poorly ventilated indoor environments (US EPA, 2021).

The development of contemporary exhibition design, characterised by frequent reconfiguration of gallery spaces and the use of new materials without prior compatibility testing, has increased the exposure of objects to acidic emissions (Lafuente et al., 2013).

This issue is exacerbated in heritage buildings repurposed as museums, where environmental conditions cannot always be adequately controlled. Original architectural features, such as vaulted ceilings or uninsulated walls, may allow the ingress of moisture and the migration of pollutants from the building materials themselves (Krupińska et al., 2013). In such cases, accelerated corrosion processes have been observed in specific areas of the objects, sometimes resulting in visible and structurally significant deterioration.

Among the most commonly identified compounds in patinas formed in indoor environments are salts such as copper(II) acetate dihydrate ($Cu(CH_3COO)_2 \cdot 2H_2O$) and copper(II) generate tetrahydrate ($C_2H_2CuO_4 \cdot 4H_2O$), which are generated through the reaction of volatile organic compounds with the metal surface, particularly under high RH conditions (Clarke & Longhurst, 1961; López-Delgado et al., 2001).

Experimental studies have shown that a concentration below 0.5 ppm of acetic acid, combined with RH levels near 80%, can trigger active corrosion of copper. This manifests in the simultaneous formation of cuprite (Cu_2O), soluble salts, and powdery copper compounds that compromise the stability of the metal surface.

Additionally, it has been identified that the presence of formic acid at concentrations starting from 100 ppm, combined with prolonged periods of high RH, can induce the formation of cuprite (Cu_2O), copper(II) hydroxide monohydrate ($Cu(OH)_2 \cdot H_2O$), and copper(II) generate tetrahydrate ($C_2H_{10}CuO_8$) (López-Delgado et al., 2001).

In summary, indoor environments, and particularly museographic ones, require specific attention from the standpoint of preventive conservation. Despite their apparent stability, they may harbour complex microclimates with corrosive effects on historical metals. The appropriate selection of materials for showcases, mounts and display systems, as well as

rigorous control of RH and ventilation, are essential measures for mitigating the risks associated with chemical degradation in these conditions.

6.1.4 Specific Corrosive Agents and Their Reaction Products

The interaction between copper alloy heritage objects and specific corrosive agents has been extensively documented in the scientific literature, highlighting several phenomena that contribute significantly to the accelerated degradation of these materials. While general environmental factors such as RH or temperature act as corrosion promoting agents, it is the specific pollutants that determine the nature and morphology of the corrosion products formed. Additionally, other factors of biological or anthropogenic origin, such as bird droppings or direct handling of the objects, also exert a significant influence on the development of corrosive processes, promoting localised and accelerated alterations. This section analyses the main agents involved in the observed corrosive mechanisms, along with the characteristic alteration products of each.

Bronze disease

Harmful patina reactions on bronze sculptures are particularly studied in archaeological objects (e.g., those recovered from burial or underwater contexts), which are especially prone to aggressive corrosion. The main alteration affecting such objects is commonly referred to as *bronze disease*.

Bronze disease typically arises in archaeological copper alloy objects at the moment of excavation. It is a phenomenon of cyclic corrosion, either marine or soil-induced, triggered

by the presence of nantokite[76] (CuCl) within the patina and its reaction with moisture and oxygen when the object is removed from its original environment (Grayburn et al., 2015; Monari et al., 2023; Robbiola et al., 1998; Scott, 1990, 2000).

This reaction leads to the formation of light green, powdery copper trihydroxychlorides, such as paratacamite or atacamite ($Cu_2(OH)_3Cl$) (Grayburn et al., 2015). Although these minerals are the catalysts, their presence alone is not a conclusive indicator of active corrosion (Scott, 1990). For the corrosion process to occur, specific environmental conditions are required, including the presence of moisture, oxygen, and a pH below 5 (Di Carlo et al., 2017; Grayburn et al., 2015).

The early identification of bronze disease is essential in the field of conservation-restoration, as its progression can rapidly compromise the structural integrity of the object (Faraldi et al., 2017). Bronze disease is a cyclic, irreversible and highly destructive form of corrosion that significantly undermines the preservation of metal artefacts, altering their surface appearance and causing structural deformations (Di Carlo et al., 2017; Faraldi et al., 2017). Even under controlled environmental conditions, the reactivation of this type of corrosion cannot be entirely ruled out, underscoring the need for continuous monitoring of affected items.

The presence of bronze disease is often indicated by light green, powdery, and voluminous spots, which serve as early visual markers of the corrosive process (Grayburn et al., 2015; Scott, 1990). The gradual formation of these corrosion products induces stress cracks on the metal surface, alters the original volume of the object, and facilitates the inward migration of chlorides, thereby exacerbating the progression of degradation (Grayburn et al., 2015).

[76] Nantokite (CuCl) is a rare copper(I) chloride that crystallises in the cubic system and appears as colourless to greyish-white crystals with a vitreous lustre. It forms in the oxidation zones of copper deposits under extremely arid conditions or as a volcanic sublimate. Highly unstable in humid air, it alters into copper hydroxychlorides such as paratacamite and is a recognised trigger of bronze disease (Hudson Institute of Mineralogy, n.db; Scott, 1990, 2002; Webmineral, n.d).

As a result, the affected areas exhibit extreme structural fragility, increasing the risk of material loss and compromising the overall stability of the object.

Acid Rain

Acid rain represents a phenomenon of particular significance in the degradation of outdoor copper alloy sculptures. This form of corrosion is associated with atmospheres of high pollution, characterised primarily by the presence of sulphur-, nitrogen- and chlorine-based compounds, as well as other acidic species. Among the principal agents responsible for the acidification of precipitation are sulphur dioxide (SO_2), sulphur trioxide (SO_3), sulphuric acid (H_2SO_4), nitrogen oxides (NO_x), nitric acid (HNO_3), chlorine (Cl_2), and hydrochloric acid (HCl), alongside organic acids such as formic, acetic, and propionic acids (Abbasi et al., 2013; Irwin & Williams, 1988). These substances, when combined with elevated levels of RH, produce acidic solutions that interact aggressively with metallic surfaces (Knotkova & Kreislova, 2007; Krätschmer et al., 2002; Robbiola et al., 1998).

Prolonged exposure to polluted environments, such as those affected by acid rain, promotes the formation of soluble corrosion products based on hydrated copper sulphates, such as chalcanthite[77] ($CuSO_4 \cdot 5H_2O$) and, more rarely, bonattite[78] ($CuSO_4 \cdot 3H_2O$) (Schlesinger et

[77] Chalcanthite is a hydrated copper(II) sulphate with the chemical formula $CuSO_4 \cdot 5H_2O$, which crystallises in the triclinic system. It typically appears as intense blue to blue-green prismatic or massive crystals, exhibiting a vitreous lustre and a hardness of 2.5 on the Mohs scale. It is a secondary mineral formed through the evaporation of copper sulphate-rich solutions, typically in arid environments or as a product of secondary alteration in copper deposits. It is highly soluble in water, which significantly limits its stability under humid conditions (Anthony et al., 2003a; Hudson Institute of Mineralogy, n.d.-b; RRUFF Project, n.d.).

[78] Bonattite is a secondary mineral composed of trihydrated copper sulphate ($CuSO_4 \cdot 3H_2O$), formed in the oxidation zones of copper minerals. In corrosion processes affecting copper alloys, bonattite may develop as a tertiary product when hydrated sulphate minerals such as brochantite or antlerite undergo alteration under conditions of fluctuating humidity and high sulphate concentration. Its presence is indicative of advanced

al., 2000; Scott, 2002). These compounds lack protective properties, are highly water-soluble, and tend to accumulate beneath existing patina layers, facilitating their disintegration. The presence of hydrated sulphates such as bonattite is typically an advanced indicator of the breakdown of the passive protective layer in copper alloys (Knotkova & Kreislova, 2007; Schlesinger et al., 2000; Scott, 2002).

In addition to sulphate formation, acid rain exerts other detrimental effects on the artwork. It alters the visual appearance, producing tarnishing and stains of greenish or reddish-brown hues, associated with the deposition of corrosive compounds (N. S. Baer & Banks, 1985; Knotkova & Kreislova, 2007).

The low pH of precipitation also promotes the leaching of minerals that constitute the patina, weakening its structure and exposing the underlying alloy to further corrosion processes (Knotkova & Kreislova, 2007; Scott, 2002; Strandberg, 1997). This phenomenon can lead to the progressive loss of the natural patina, thereby compromising the aesthetic and historical legibility of the object. In advanced stages, leaching may result in the disappearance of entire superficial strata, exposing bare metallic surfaces that are highly vulnerable.

Moreover, it has been demonstrated that copper released through runoff from exposed architectural surfaces, such as roofs and façades, can accumulate on adjacent materials including soil, stone or concrete, altering their surface composition and increasing the bioavailability of copper compounds in the immediate environment. These findings are applicable to outdoor bronze sculptures, where similar processes of copper deposition and accumulation may occur on plinths or bases (Hedberg et al., 2014).

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stages of corrosion associated with sulphated atmospheric environments (Hudson Institute of Mineralogy, n.d.c; Scott, 2002).

From a structural perspective, acid rain promotes the development of generalised corrosion, with the deposition of soluble salts, and chemical dissolution processes affecting both the patina and the metallic substrate. If undetected and untreated, these alterations may evolve into cracking, loss of density, reduced mechanical strength, and diminished ductility of the metal (Chiavari et al., 2007; Knotkova & Kreislova, 2007; Revie & Uhlig, 2008; Sharif-Askari & Abu-Hijleh, 2018; Strandberg, 1997).

The severity of these effects varies according to multiple factors, including the frequency and intensity of acid rain, the local microclimate, the composition of the alloy, and the pre-existing conservation state of the patina. Particularly vulnerable are works located in densely industrialised urban environments or in close proximity to pollutant emission sources.

Black Crust Formation and Environmental Deposits

Another critical manifestation of environmental corrosion on bronze sculptures is the formation of black crusts, which result from the cumulative action of various pollutants. These encrustations, while often overlooked, represent a significant alteration product and are particularly prevalent in urban and industrial contexts.

Black crust is a superficial encrustation that frequently forms on outdoor bronze sculptures. It commonly appears in polluted atmospheres as dark stains, black spots or opaque, enamel-like layers, often with a glassy appearance. Its presence represents not only a significant aesthetic alteration, as it masks original colours and modifies forms and textures, but also a potential risk to the structural integrity of the object.

Several authors have documented the frequent incorporation of airborne particles such as alumina, silica, iron oxides and soot into the altered patinas of exposed sculptures. These particles adhere to the surface and act as nucleation sites, consolidating dense and opaque layers characteristic of black crusts. Rather than being mere passive accumulations, they interact actively with copper corrosion products.

Among these, soot plays a particularly significant role in darkening the surface and retaining moisture, creating acidic microenvironments that promote corrosion. This phenomenon is intensified by atmospheric sulphur dioxide (SO_2) and particulate matter, especially in areas subject to cyclic wetting and drying. Rough or microcrystalline patina surfaces act as efficient traps for pollutants, enhancing their retention and accumulation (Graedel et al., 1987; Gullman & Törnblom, 1994; Pichler & Kautek, 2025; L. Selwyn, 2004).

From a chemical perspective, these crusts result from the reaction between copper corrosion products, such as sulphides, oxides and cuprite, and the aforementioned airborne particles. These include combustion residues, gypsum (calcium sulphate), basic copper sulphate and other carbonaceous particles. Small quantities of sulphides have also been detected, possibly originating from old artificial patinas or urban contaminants such as tyre dust. These formations can reach several millimetres in thickness and display a highly heterogeneous structure, ranging from loose, porous deposits to dense, compact, insoluble layers (Weil, 1974).

Cross-sectional analyses typically reveal two distinct layers: a thin, crystalline lower layer composed of calcium carbonate and gypsum; and a thicker, darker upper layer, rich in silica. The mineralogical composition is complex, including iron hydroxy-sulphates, free quartz, copper sulphides and sulphates, aluminium silicate and trace amounts of iron, titanium and manganese (Weil, 1974).

Hydrochloride compounds such as atacamite have also been identified, particularly in the form of localised pitting. These compounds can arise not only from marine influence, but also from industrial aerosols, the combustion of chlorinated materials such as PVC, or inappropriate conservation interventions. For instance, the use of hydrochloric acid in cleaning processes, if not properly neutralised, may leave chloride residues that migrate through the patina. Similarly, some green patina formulas contain ammonium chloride, which encourages the formation of secondary chloride-based compounds (Heuman, 1992).

Beyond their visual impact, black crusts function as active agents of deterioration. By retaining acidic moisture, they can induce localised corrosion and promote pitting

phenomena, compromising the underlying metal (Riederer, 1972, as cited in Weil, 1974). Their removal is especially challenging due to their strong adherence; often requiring controlled mechanical procedures such as scraping or advanced techniques like laser cleaning (Di Francia et al., 2022; Koh, 2006; Sansonetti et al., 2015; Zanini et al., 2018).

Excreta-Induced Corrosion

Corrosion caused by bird excrement constitutes one of the most frequent causes of both aesthetic and structural deterioration in artworks made from copper alloys. The chemical composition of excrement not only promotes corrosion processes but can also significantly accelerate the degradation of affected objects (Balogh, 2017; Bernardi, Bowden, et al., 2009; Vasiliu & Buruiana, 2010). Such damage is particularly severe in environments with elevated levels of sulphur dioxide (SO_2) and high RH. Conversely, in atmospheres with low SO_2 content, the incidence of damage decreases, although the aggressive effect of chloride salts on the metallic surface persists (Balogh, 2017; Balogh et al., 2017; Knotkova & Kreislova, 2007).

Controlling this type of corrosion presents considerable challenges, largely due to the high presence of birds, particularly pigeons and seagulls, in urban environments. Their presence is significantly greater in areas with high tourist activity, where food sources are abundant, and concentrations of historical monuments are high. Although a variety of strategies have been implemented, such as the use of auditory deterrent devices or the introduction of trained birds of prey, these methods have proven to be merely palliative, failing to offer a sustainable long-term solution.

Bird excrement consists of a mixture of faeces (dark in colour) and urinary waste (white in colour), expelled together through the cloaca (Jacob & Pescatore, 2013). Gómez-Heras et al. (2004) report that this mixture contains insoluble organic and inorganic compounds, along with various salts, including phosphates, chlorides, sulphates, fluorides, bromides, and

nitrates. Additionally, bacteria and fungi are commonly present (Bassi & Chiatante, 1976; Huang & Lavenburg, 2011).

Among the components of bird excrement, uric acid and copper oxalates stand out as particularly aggressive agents in the degradation of bronze patina. Uric acid, the principal component of avian urinary waste, undergoes degradation that produces ammonia, which is subsequently nitrified, thereby intensifying corrosive activity (Balogh, 2017; Balogh et al., 2017, 2019; McNabb, 1974; Vasiliu & Buruiana, 2010). Upon contact with the metal surface, uric acid reacts with the patina, generating a new layer which, although it may initially act as a protective barrier, profoundly alters the passivity and chemical stability of the original patina (Vasiliu & Buruiana, 2010). The formation of darkened layers, facilitated by sustained moisture, promotes the continuation of electrochemical corrosion processes (Bernardi, Bowden, et al., 2009).

Hydrated copper oxalates[79] ($CuC_2O_4 \cdot nH_2O$) can form as degradation products of malachite ($Cu_2CO_3(OH)_2$) under environmental conditions enriched in organic acids, particularly oxalic acid produced by biological activity (Castro et al., 2008). Their presence on outdoor artworks indicates an advanced stage of deterioration, often associated with prolonged exposure to bird droppings and intense microbiological colonisation (Castro et al., 2008; Fujisawa & Hemuki, 2019; Knotkova & Kreislova, 2007; Scott, 2002).

These processes not only reveal the vulnerability of historic surfaces to biological contaminants, but also underscore the urgency of adopting more proactive conservation strategies. Addressing the effects of corrosion induced by bird excrement requires integrating measures that combine urban wildlife management with specific actions for the

[79] Hydrated copper oxalates ($CuC_2O_4 \cdot nH_2O$) are corrosion products that form through the interaction of copper-based surfaces with oxalic acid, typically in biologically active environments. These compounds are frequently associated with the degradation of bronze or copper alloys exposed to organic matter such as bird droppings, lichens, or microbial biofilms, and are considered indicators of biocorrosion (Castro et al., 2008; Fujisawa & Hemuki, 2019; Scott, 2002).

protection of exposed materials, thereby reinforcing the resilience of cultural heritage against a type of alteration often underestimated in conservation policies.

Handling-Induced Corrosion

Handling-induced corrosion particularly affects copper and copper alloy objects that lack a natural or artificial protective patina and are subject to frequent contact, such as door handles, railings, or medical instruments. This phenomenon occurs due to the transfer of sweat and sebum from human hands to the metal surface.

Sweat consists predominantly of chloride, sodium and potassium ions, as well as urea, lactic acid, and traces of nitrates, phosphates and sulphates (Fredj et al., 2013; Hostýnek, 2004; Lind, 1972). Among these components, sodium chloride residues are the primary agents responsible for corrosion, while lactic acid and urea contribute to a lesser extent. The severity of the corrosive attack increases significantly under conditions of high RH (Lind, 1972).

Areas affected by handling tend to darken and develop a matte finish, losing the characteristic lustre of unpatinated bright metal. Without appropriate preventive conservation measures, these zones deteriorate further, leading to the development of surface roughness and pitting (Fredj et al., 2013).

The analysis of handling-induced corrosion, together with the processes examined in the preceding sections, highlights the variety of environmental, human, and animal factors involved in the alteration of copper alloys used in heritage objects. This evidence points to the need for conservation strategies that consider not only atmospheric agents but also everyday interactions with objects, often overlooked but with a cumulative and significant impact on their preservation.

In this regard, existing studies on corrosive agents and alteration products provide a useful basis for interpreting the condition of sculptures made from these alloys. In the following section, this knowledge will be applied to the analysis of specific case studies, which will

examine the environmental conditions, constituent materials, and the museographic or urban contexts in which the works are situated. This transition from theoretical framework to direct object examination will allow for a technically grounded analysis of the relationship between alterations observed during fieldwork and corrosion products identified in the analytical study.

6.2 CORROSION FACTORS OBSERVED IN THE STUDY OBJECTS

An understanding of the corrosion mechanisms outlined in the previous section forms the basis for interpreting the deterioration processes observed in the sculptures selected for this study. This section identifies and examines the environmental, biological, and handling-related factors that have affected the objects, assessing their impact in relation to exposure conditions, constituent materials, and documented past interventions. This comparative analysis will allow for the establishment of causal relationships between alteration agents and the current condition of the sculptures, providing a critical foundation for the subsequent discussion on preventive conservation and restoration strategies.

6.2.1 Influence of Humidity and Temperature on Corrosion Processes

Environmental factors have played a decisive role in shaping the deterioration processes observed in the analysed copper alloy sculptures. Exposure conditions, both outdoors and indoors, have significantly influenced the nature and rate of corrosion phenomena affecting metallic surfaces. This section examines the main environmental agents identified, with

particular attention to RH, temperature fluctuations, atmospheric pollutants, and the potential influence of marine aerosols (Robotti et al., 2018).

RH and temperature are critical modulators of corrosion rates (Cai et al., 2018). Fluctuations in these parameters, particularly in outdoor environments, promote wetting and drying cycles, which activate electrochemical processes on the metal surface. High RH levels facilitate the dissolution of soluble salts and the mobility of aggressive ions such as chlorides and sulphates, exacerbating the instability of surface layers.

The ability of metallic surfaces to adsorb water plays a fundamental role in this process. According to Graedel et al. (1987), at 60% RH and a temperature of 20 °C, copper adsorbs approximately 15 monolayers of water, increasing to 27 monolayers at 90% humidity. The adsorbed water film acts as an electrolyte even under moderate humidity conditions, promoting the dissolution of passive protective oxide layers and initiating corrosion. The presence of reactive substances, such as chlorides, intensifies this phenomenon by weakening the passive layer and favouring localised reactions (Strandberg, 1997).

Thermal fluctuations also contribute to the deterioration of sculptures. The cyclical expansion and contraction of metals induce mechanical stress in both the patina layers and the underlying metallic structures. Although these changes may be imperceptible to the naked eye, their cumulative effect gradually alters the physicochemical behaviour of the surface (Grattan & Michalski, 2017).

In outdoor environments, in addition to typical seasonal variations, the increasing impact of recent climate change has been observed, characterised by abrupt and unpredictable fluctuations in temperature and humidity over short periods (Leygraf et al., 2016). These environmental dynamics intensify surface stress processes and contribute to the destabilisation of patina layers, weakening their protective capacity against new corrosive agents.

6.2.2. Guimarães: Stable Environmental Exposure and Low Industrial Influence

In the analysis of the statue of *King Afonso Henriques* in Guimarães, the corrosion products identified reflect moderate interaction with the surrounding environment, consistent with prolonged exposure in an urban context with low industrial pollution and no direct influence from the marine atmosphere. The detection of cassiterite (SnO_2) and other tin oxides indicates that the copper alloy used contains tin as a compositional element, and as explained in Section 6.1.2, its formation gives rise to a passive layer with high chemical stability. This layer has proven effective in reducing the corrosion rate of underlying copper oxides, suggesting a protective response of the material in certain areas of the sculpture.

In addition, the significant presence of cuprite (Cu_2O) as the main product of initial oxidation confirms the development of a stable and adherent patina, typical of copper alloys exposed to environments with low SO_2 concentrations (Strandberg, 1997). This type of formation is consistent with the environmental characteristics of the area, where no major SO_2 emission sources are recorded, nor is there evidence of chloride-based agents typically associated with coastal or industrialised zones.

Although Guimarães is classified as having a temperate oceanic climate (Csb) according to Köppen-Geiger, its location among mountain valleys limits the direct entry of marine aerosols (Agencia Estatal de Meteorología, 2011). This geographic condition, combined with the absence of large-scale industrial activity, explains the lack of detected chloride-based compounds such as nantokite, atacamite, or paratacamite on the analysed surfaces.

Moreover, Guimarães is among the regions with the highest rainfall in mainland Portugal, a characteristic it shares with southern Galicia and other areas in the north-west of the Iberian Peninsula. Annual precipitation ranges between 1500 and 2000 mm, and RH rarely drops below 60% in summer, averaging over 85% during the winter months (Agencia Estatal de Meteorología, 2011; Instituto Português do Mar e da Atmosfera, 2015). The city's relative proximity to the Atlantic Ocean also acts as a thermal buffer, helping to moderate extreme temperatures. The average minimum temperature during the coldest months is 8 °C, rarely

falling below 0 °C, with a January mean minimum of 4.5 °C. In the warmest months, the general average temperature is 20.2 °C, reaching an average of 27.2 °C on the hottest days of July. These conditions define a low thermal aggressiveness environment (Guimarães Turismo, n.d.).

These conditions, namely, the presence of humidity and solar radiation capable of raising the surface temperature of the copper alloy, favour the formation of hydrated and sulphur-based corrosion products such as posnjakite and brochantite. The presence of these compounds on the sculpture suggests prolonged interaction with a moderately sulphur-contaminated environment. Posnjakite, a hydrated and unstable mineral, tends to form from cuprite in low-sulphur environments and at moderate surface temperatures, typically between 20 and 50 °C. As thermal conditions increase, it may progressively transform into brochantite, which crystallises more stably from around 80 °C, provided the ambient pH remains close to 7.5. Tenorite, identified on the sculpture's sword, requires slightly higher concentrations of sulphur compounds and a pH above 8.5; its formation is associated with the whitish areas observed in Figure 5.14 of Chapter 5. Although these sulphates and oxides are less stable than cuprite or cassiterite, their occurrence is consistent with the climatic characteristics of Guimarães and long-term exposure to non-aggressive environmental conditions (Krätschmer et al., 2002; Zittlau et al., 2013). These findings support the identification of a Type I patina, according to the classification proposed by Robbiola et al. (1998).

6.2.2.2 Porto: Outdoor Sculptures Subjected to Urban and Marine Atmospheric Stress

In the analysis of the sculptures located in outdoor spaces in the city of Porto, the analytical results reveal a greater diversity and aggressiveness of corrosion products compared to the statue studied in Guimarães. In particular, the busts of *Francisco de Almada e Mendonça* and *João Marques de Oliveira*, as well as the sculpture *Figura Feminina*, present compounds indicative of interaction with a coastal urban environment, marked by exposure to marine aerosols, high RH, and pollutants of urban and industrial origin.

Porto is characterised by a temperate oceanic climate (Csb according to Köppen-Geiger), strongly influenced by its direct exposure to the Atlantic Ocean, which largely determines its climatic conditions (Agencia Estatal de Meteorología, 2011; Alcoforado, 1998). The annual average temperature is around 14 °C, with summer highs reaching 24 °C and winter lows around 6 °C, rarely falling below 1 °C (Agencia Estatal de Meteorología, 2011).

Relative humidity remains high throughout the year, ranging from 73% in summer to 81% in winter. Annual rainfall exceeds 1200 mm, with December and January recording the highest values (above 150 mm) and July and August the lowest (below 50 mm). The number of days with precipitation is close to 150, many of them with totals of less than 10 mm (Agencia Estatal de Meteorología, 2011; Góis, 2002; Ramos, 2000). Air masses arriving directly from the Atlantic act on the coastline as a primary barrier, modifying the physical characteristics of rainfall as well as its humidity, direction and speed (Góis, 2002). Urban relief also plays a significant role: the higher areas of the city are wetter than both the coastal zone and the southern bank of the Douro River, since the river channels the entry of oceanic air masses and hinders their ascent (Daveau, 1977, apud Góis, 2002).

The coldest months are January and February, when the lowest mean temperatures are recorded, whereas the warmest months occur in July and August, with values tempered by the maritime influence that prevents extreme conditions. These features are complemented by abundant rainfall and high atmospheric humidity, factors that contribute both to the relative coolness of the summer and to the damp sensation experienced in winter, thus defining a seasonal dynamic characterised by mild winters and moderate summers (Monteiro, 1998). Fog is another distinctive climatic feature, with around 120 foggy days per year, evenly distributed but peaking in August and December. Its occurrence is linked both to the proximity of the Atlantic and to the Douro River, which together create favourable conditions for its formation (Góis, 2002).

In addition, the winter meteorological conditions of Porto, driven by Atlantic influence, atmospheric pressure, temperature and frequent rainfall, generally allow for a relatively effective dispersion of air pollutants (CCDR-N & FCT NOVA, 2021). Even so, the city has

long been subject to sustained environmental pressure from decades of industrial, vehicular, and residential activity, releasing compounds such as CO_2, NO_2, SO_2, hydrocarbons, and Pb into the urban atmosphere. Porto, in particular, has been marked by high levels of airborne particulate matter, largely resulting from industrial, automotive, and domestic combustion. Among these factors, the widespread use of low-occupancy private vehicles stands out as a major contributor to the emission of persistent pollutants (Monteiro, 2001).

However, between 1990 and 2020, emissions decreased by 66%, mainly due to a 91% reduction in sulphur dioxide (SO_2), a 51% reduction in nitrogen oxides (NO_x), and a 22% reduction in ammonia (NH_3) (Direção Municipal de Urbanismo, 2018; Portal do Estado do Ambiente, 2024). This positive trend reflects a progressive reduction of environmental pressure on the city's metal heritage.

The bust of *João Marques de Oliveira* showed only cuprite and an alloy of cobalt, copper, and tin. The sculpture has been subject to frequent cleaning due to vandalism involving paint, resulting in the periodic removal of surface layers. As a result, the observed corrosion is relatively recent and corresponds to early oxidation processes. The black coloration of the surface may be linked to the presence of an original artificial patina. Additionally, the detection of cobalt and tin may be related to the chemical composition of the spray paint used in the acts of vandalism, although it is also possible that the tin originated from the copper alloy itself, as a by-product of localised corrosion processes. The presence of cuprite suggests that the environment where the sculpture is located, similar to that of the other analysed works, does not exhibit high levels of atmospheric pollution, allowing for the formation of this oxide typical of low-pollution settings.

On the bust of *Francisco de Almada e Mendonça*, corrosion compounds such as brochantite, antlerite, and atacamite were identified, indicating alteration processes linked to atmospheric sulphur and chloride compounds. Brochantite forms in neutral to slightly alkaline conditions, whereas antlerite, more common in acidic environments, may be associated with the action of urban pollutants. The presence of atacamite, a copper chloride, confirms the possible influence of marine aerosols on the alloy surface (Cramer et al., 2002).

In the sculpture *Figura Feminina*, the simultaneous presence of cuprite and atacamite, along with phosphates and silicon oxides, suggests a scenario of passive oxidation altered by the action of chlorides and airborne particulates. The penetration of these agents into the passive layer has favoured the progression towards more active forms of corrosion.

The outdoor environment of Porto, characterised by high RH, the presence of saline aerosols, and intense urban activity, favours the formation of corrosion products typical of marine-urban settings. Although the analysed sculptures are located several hundred metres from the coastline, the city is not immune to the influence of salt-laden mist from the Atlantic Ocean. This atmospheric phenomenon, associated with suspended marine salts in the form of fog or fine aerosol, can be transported inland by wind, especially through open geographical structures (Q. Chen et al., 2024; Xiang et al., 2023). In this context, the course of the Douro River acts as a natural corridor, facilitating the inland movement of salt mist into urban areas, allowing marine aerosols to reach zones that would otherwise be relatively sheltered from direct marine action.

Studies have shown that the concentration of dissolved salts in the mist gradually decreases as one moves inland from the coast. This reduction is intensified by factors such as distance from the sea, relative terrain elevation, and the presence of architectural barriers that obstruct marine breeze circulation (Morcillo et al., 2000; Tang et al., 2023). In this case, the studied sculptures are located only a few hundred metres from the riverbank, which increases the likelihood of exposure to airborne chlorides channelled through the river's path. This condition could explain the appearance of chloride-based corrosion products such as atacamite even in works situated far from the seafront.

In this environmental context, compounds such as atacamite reflect more active and less stable corrosive processes that compromise the durability of copper alloy surfaces present in the studied sculptures. Atacamite, a copper chloride, serves as a direct indicator of marine aerosol action on these metal surfaces. This mineral naturally forms in former saltworks or hypersaline environments under prolonged arid conditions (Hudson Institute of Mineralogy, n.d.-a). In the case of Porto, its presence may be related not only to airborne salt deposition,

but also to the drier conditions typical of the summer months. During these periods, marked by low precipitation and high solar radiation, conditions become favourable for the surface crystallisation of chlorides such as atacamite, forming from concentrated saline solutions in contact with copper alloy surfaces (Cramer et al., 2002; Lan et al., 2008; Lopesino et al., 2018).

The variety and nature of the corrosion products identified in the outdoor sculptures of Porto demonstrate the complex interaction between local environmental conditions and heritage metal materials. The combination of high humidity, temperature fluctuations, and repeated wetting and drying cycles has favoured differentiated alteration processes, some of which may evolve into forms of corrosion that threaten the long-term stability of the alloy. This dynamic is consistent with the findings of Strandberg (1997), who emphasised that successive wet-dry cycles act as catalysts in the dissolution of passive products and in the reactivation of active corrosive processes. This scenario calls for a preventive conservation approach, one that is sensitive both to the material history of each work and to the environmental dynamics of its location.

6.2.2.3 Porto: Indoor Sculptures in Museum Environments with Variable Microclimates

The analysis of sculptures located in indoor spaces in the city of Porto, specifically the devotional figures of S. José and S. Joaquim, both housed at the MNSR, reveals a corrosion dynamic distinct from that observed in outdoor sculptures. Although situated in a museum context, the analytical results show that interior conditions have not fully ensured the chemical stability of their metal surfaces.

These sculptures were traditionally displayed in the sculpture gallery on the first floor of the museum, known as the Soares dos Reis Gallery, a space with direct access to both the temporary exhibition hall and the garden, connected via glass doors that are occasionally opened on warm days. While the gallery is equipped with forced ventilation, the circulating air passes only through particle filters and lacks active climate control or specific regulation of RH, allowing for certain microclimatic fluctuations.

During the museum’s renovation works, completed in 2024, both sculptures were removed from display and relocated to the museum's storage areas. There, they shared space with objects of various material compositions, under typical temporary storage conditions. One of the samples analysed, from the sculpture of S. José, was taken during this period from a non-visible area of the object coated with an artificial brown patina. This context may have influenced the recorded chemical composition, particularly given the material diversity in the environment and the variable conditions at that time. It should also be noted that following the gallery’s refurbishment, the sculptures of S. José and S. Joaquim were not reinstated in the exhibition space and have remained in storage since then.

In the sculpture of S. José, XRD analysis revealed the presence of cuprite, brochantite, and quartz, although their distribution varied between samples. In the green-coloured sample, brochantite, cuprite, and quartz were identified, suggesting interaction between the metal and sulphur-based agents under moderate temperature and humidity conditions, typical of non-climatised indoor environments. In the dark brown sample, associated with an artificial patina, only cuprite and quartz were detected, with no sulphates present. This may indicate reduced direct environmental exposure or the presence of a previously applied protective layer. The occurrence of cuprite in both samples reflects the low level of atmospheric pollution in the indoor environment, while the quartz may be linked to environmental deposits or airborne mineral particles.

In the case of S. Joaquim, the results revealed greater complexity and surface heterogeneity. Cuprite, atacamite, and posnjakite were identified, alongside non-metallic materials such as paraffin, silicon phosphate, and hydrated barium chloride. The sample was collected while the sculpture was still on display in the Soares dos Reis Gallery, allowing the detected products to be associated with the specific environmental conditions of that space. The presence of atacamite suggests potential exposure to saline aerosols, although its occurrence in closed interior environments is uncommon. Recent studies indicate that the penetration of salt-laden mist is significantly reduced inside buildings, which limits the likelihood of direct deposition of marine salts onto indoor metal surfaces (Tang et al., 2023).

Posnjakite forms under moderate RH and surface temperatures close to 50 °C. Being an unstable mineral, its presence suggests recent corrosion processes, as it tends to transform into brochantite over time or in response to increased thermal conditions.

The detection of paraffin may indicate the presence of a previous conservation treatment or protective application. Silicon phosphate and hydrated barium chloride may be associated with environmental deposition processes. The combination of these compounds highlights the chemical complexity that can develop on metal surfaces even in museum environments, where ambient conditions and conservation practices directly influence the evolution of corrosion products.

It should be noted that this study did not include the specific analysis of VOCs such as formaldehyde, acetic acid, or formic acid, which are commonly present in museum settings due to emissions from materials such as wood, varnishes, or resins. This omission is due to the inherent limitations of XRD, which identifies crystalline structures based on their diffraction patterns. Since acetic and formic acids are volatile liquids under normal conditions and do not easily crystallise, they do not produce stable diffraction signals, particularly when present as vapours or absorbed into porous materials. Although XRD can detect secondary reaction products associated with these acids, such as certain metal salts, it is not effective for identifying the acids themselves, meaning their potential impact on the sculptures could not be assessed directly in this analysis.

However, in her doctoral thesis, Barbosa (2023) conducted a study on the presence of volatile organic compounds in several Portuguese museum institutions, including the MNSR. In the case of the Soares dos Reis Gallery, VOCs were collected using Tenax TA adsorption tubes and subsequently analysed by gas chromatography with mass spectrometric detection (GC/MSD). In parallel, formaldehyde levels were measured using SKC 500-100 UMEx 100 devices, analysed via high-performance liquid chromatography (HPLC). Suspended particulate matter was monitored with a Dusttrak DRX Aerosol Monitor 8533.

Barbosa's results showed that, while no formaldehyde was detected in the Soares dos Reis Gallery, acetic acid was identified at concentrations of 5.08 and 5 μg/m³ in the two zones

analysed. Additionally, total VOCs concentrations reached 209 and 65.1 μg/m³, confirming a significant volatile organic load in the environment. These data provide valuable context for the indoor atmospheric conditions to which the sculptures were exposed and open new lines of investigation regarding the cumulative effects of such compounds on heritage metal materials.

Acetic acid, in particular, is a common and highly reactive indoor pollutant, released by materials such as paints, varnishes, adhesives, silicones, and woods, especially cedar and oak. In combination with sodium ions, it can result in the formation of white efflorescence such as sodium acetate trihydrate and promote copper corrosion, leading to the formation of greenish copper salts (Barbosa, 2023; Tennent & Baird, 1992; Tétreault, 2003).

Taken together, the analysis of indoor sculptures at the MNSR demonstrates that even within museum settings, non-stabilised environmental conditions and the possible interaction with complex volatile compounds can trigger unanticipated corrosion processes. This scenario aligns with effects observed in museum contexts where VOCs emissions are present, as discussed in Section 6.1.3, and underscores the importance of systematic environmental monitoring and further research on secondary corrosion products, particularly in storage or exhibition contexts.

6.3 FINAL REMARKS ON CHAPTER 6

The results presented in this chapter confirm that corrosion processes in copper alloy sculptures cannot be understood independently of their specific environmental contexts. While specialised literature provides a solid interpretative framework for the alteration products observed, the case studies demonstrate that local factors, whether urban, coastal, or museographic, generate complex and often unpredictable material responses, which are

difficult to anticipate without an integrated analysis of environmental conditions, historical-material characteristics, and past interventions.

In particular, the comparison between outdoor and indoor sculptures highlights that the categories of *aggressive environment* or *controlled setting* are not absolute. On the contrary, seemingly stable environments such as museum spaces can host microclimates capable of triggering active corrosion, resulting from interactions between volatile organic compounds, uncontrolled humidity, and display or packaging materials.

Moreover, the mineralogical analysis of the metal surfaces shows that certain corrosion products, such as atacamite, posnjakite, or brochantite, not only reflect past environmental conditions but also help anticipate possible degradation pathways if appropriate preventive measures are not implemented.

From this perspective, knowledge of specific corrosive agents and their reaction products should not be limited to diagnostic purposes. Rather, it must be actively integrated into conservation strategies, both at the level of exhibition planning and in the management of sculptures displayed in urban environments. This chapter has provided a critical foundation for such integration, essential to guiding preventive conservation and restoration decisions, as developed in the following chapter.

PART III CONSERVATION RESTORATION OF COPPER ALLOYS

INTRODUCTION TO PART III

Como se tratasse de promover n'esta cidade uma solemnidade patriótica por occasião do anniversario do dia 9 de julho, entendeu-se que o monumento de D. Pedro IV devia ser limpo e assim mandou-se lavar e escovar o bronze da estatua, de modo que o que tanto anno custa a conseguir, isto é a oxidação que imprime esta beleza preciosa aos bronzes antigos, julga-se entre nós uma cousa suja, impropria! [...] Já que a ignorancia faz praticar tanto disparate, fique-se sabendo: Que os bronzes nunca se limpam.

As an attempt was made in this city to promote a patriotic celebration on the occasion of the anniversary of July 9th, it was decided that the monument to Dom Pedro IV should be cleaned. Thus, the bronze of the statue was ordered to be washed and brushed, in such a way that what takes many years to develop, namely, the oxidation that lends ancient bronzes their precious beauty, is here considered something dirty, improper! [...] Since ignorance leads to such foolishness, let it be known: bronzes must never be cleaned.

— Manoel M. Rodrigues, *A Arte Portugueza*, July 1882

The preservation of metallic artefacts has represented an evolving challenge throughout history, generating intense debates both among conservation professionals and the general public, particularly in relation to the retention or removal of natural patina (Micheli, 2015).

In Portugal, this controversy has sparked heated discussions since the 19th century, particularly within cultural circles, as evidenced by the previously cited excerpt by Manoel Rodrigues (1882b), a journalist and friend of Soares dos Reis, published in *A Arte Portuguesa*. This passage illustrates the polarisation of opinions surrounding the conservation or removal of patina on sculptures, highlighting the complexity of the issue.

The appreciation of patina as an aesthetic element dates back to Antiquity, when it was regarded as a symbol of beauty and dignity acquired over time. From an artistic perspective, it is argued that patina should be preserved not only for its protective properties but also as a witness to the temporal evolution of the work, an argument supported by the field of conservation-restoration (L'héronde et al., 2019).

Within the field of conservation, it is essential to balance the preservation of a piece's historical integrity with the need to halt or prevent the advancement of corrosion. This task requires complex decision-making regarding whether a corrosive patina should be removed or preserved as part of the object's history.

The complexity of this challenge is further heightened by the various forms of corrosion arising from pollution, a phenomenon intensified since the Industrial Revolution and exacerbated by new contaminants in urban and industrial environments. Added to this are the thermal and humidity fluctuations attributable to climate change, which have increased the aggressiveness of corrosive agents.

In response, growing environmental awareness has driven the search for materials that ensure safe treatments for conservation-restoration professionals, the environment and the artworks themselves, while upholding the principle of reversibility, a cornerstone of contemporary conservation.

In this context, environmental factors and their variations, particularly those linked to climate change, are key in shaping the development of both stable and harmful corrosion. As discussed in Chapters 5 and 6, the location of sculptural works plays a decisive role in the nature of corrosion affecting them.

A clear example is the monument to *King Afonso Henriques* in Guimarães, situated in an open environment, far from the sea and with low industrial activity, which displays stable corrosion products according to XRD analysis. By contrast, sculptures located in Porto, including those housed within the MNSR, exhibit chloride hydroxides, attributed to both the city's industrial activity and its proximity to the sea.

Most conservation treatments applied to metallic artefacts involve cleaning, passivation and surface protection (Robbiola, Fiaud, & Pennec, 1993). In this Part 3, two complementary approaches are examined: first, the conservation-restoration practices documented through an international questionnaire (Chapter 7), and second, the contemporary techniques applied to bronze conservation, together with the sustainable methods currently under investigation to make conservation "greener" and safer for both professionals and the environment (Chapter 8).

Although it is not feasible to establish a universal restoration protocol for bronze sculptures, it is possible to define fundamental diagnostic and preventive conservation guidelines. These principles must always consider the historical, environmental and material context of each object. The critical reflection developed throughout this Part 3 will demonstrate how professional decisions in practice respond, or fail to respond, to these criteria, and which challenges remain to consolidate sustainable and ethically responsible approaches to bronze conservation.

CHAPTER 7. SURVEY ON BRONZE CONSERVATION PRACTICES

The conservation and restoration of metals, particularly bronze, is a field in constant evolution within the discipline of cultural heritage conservation. Over the past decades, increasingly sophisticated intervention protocols have been developed, which has led to significant progress in the understanding of alteration processes and in the methodologies to address them. Nevertheless, important challenges and methodological limitations persist, which underline the need for a critical evaluation of current practices.

Despite scientific and technological progress, uncertainty still remains regarding the suitability, long-term effectiveness, and sustainability of certain treatments. In this regard, recent research has begun to focus on environmentally responsible conservation strategies, aimed at reducing the ecological footprint of interventions and minimising the use of hazardous chemicals. This change of perspective reflects a growing commitment to methods that seek to be both effective and sustainable.

However, the application of these methodologies varies considerably among conservator-restorers, museums, public institutions, and foundries, which shows a lack of homogeneity in protocols and criteria of intervention. This diversity of approaches makes it necessary to obtain a clearer vision of the current state of professional practice, both in terms of diagnostic processes and in treatments and preventive measures.

In order to contextualise the challenges outlined above and to obtain a broad view of contemporary practice, an international questionnaire was distributed among conservators-restorers, museums, public institutions, and art foundries. Its purpose was to document the principal deterioration problems affecting bronze sculptures, as well as the diagnostic methodologies, conservation treatments, and preventive strategies currently employed, with particular attention to sustainable approaches.

The following subchapters present the results of this survey. The information is organised around the main themes addressed in the questionnaire: the professional and institutional profiles of the participants, the types of sculptures most frequently treated, the deterioration phenomena identified, the diagnostic techniques employed, the conservation and restoration methods reported, and the preventive measures linked to sustainability. Beyond the technical data, these results provide insight into the diversity of current practices and highlight the shared challenges that characterise bronze conservation today.

7.1 DESIGN AND OBJECTIVES OF THE BRONZE CONSERVATION QUESTIONNAIRE

The questionnaire, available in English, Portuguese, Spanish, and French, was distributed internationally to museums, public institutions, conservation-restoration companies, art foundries, and freelance professionals. Structured in 12 sections, it addressed deterioration assessment, preliminary analyses, cleaning, consolidation, repatination, preventive conservation, and sustainability.

Its design allowed the flow of questions to adapt to each respondent's profile, combining closed, multiple-choice, and open-ended questions in order to capture both standardised data and more nuanced professional perspectives. Key topics included treatment criteria for

patina and base metal alterations, the applicability of traditional and innovative methods (such as laser ablation), and the awareness and application of sustainable practices.

The complete questionnaire is included in Appendix C.1. Its structure provided a representative overview of current professional practice and helped identify common approaches, gaps, and areas requiring further research, particularly in the fields of sustainable materials and preventive strategies.

7.2 RESPONSE RATES AND DATA RELIABILITY

Of the 89 valid questionnaires, 71 (79.8%) were completed either fully or to a high degree (more than 50% of questions answered). This group, comprising 63 fully completed responses and 8 high-level partial responses, provides the most reliable basis for analysis due to the consistency and detail of the information supplied (Figure 7.1).

Three questionnaires were entirely blank and were excluded from the analysis. To assess the representativeness of the dataset, responses were classified by completion level:

- Low partial responses (1–9%): 9 entries
- Medium partial responses (10–49%): 9 entries
- High partial responses (50–99%): 8 entries
- Complete responses (100%): 63 entries

The high proportion of complete responses (70.8%) constitutes a robust dataset for cross-comparison between institutions, regions, and professional approaches.

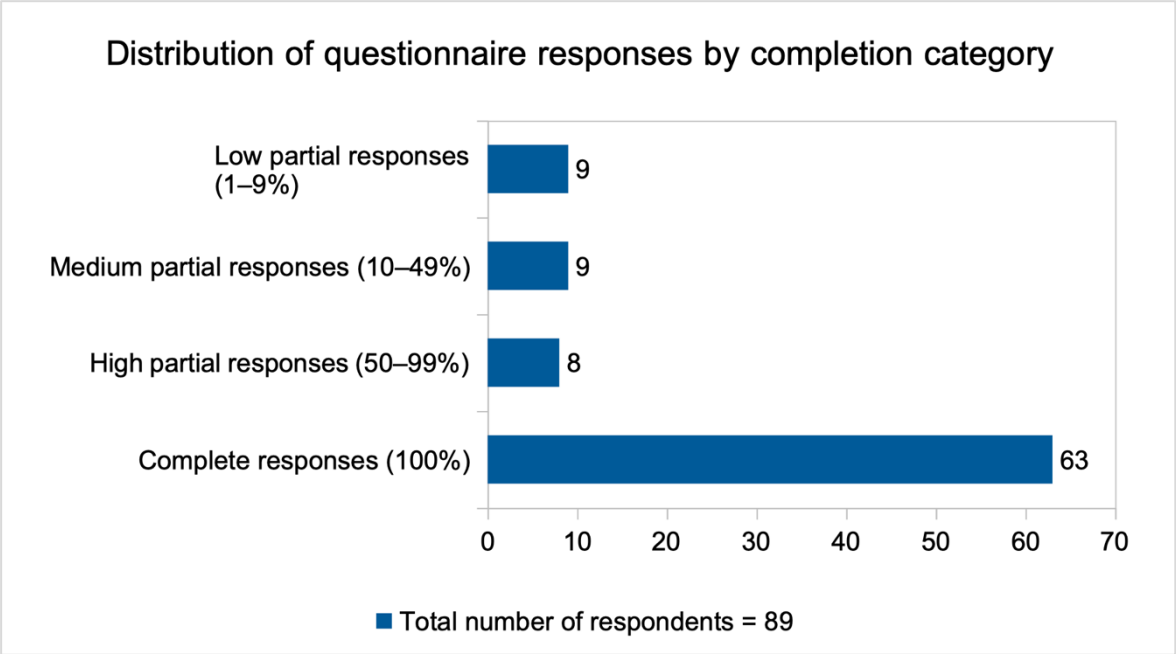


Figure 7.1 - Distribution of questionnaire responses by completion category.

7.3 GEOGRAPHICAL DISTRIBUTION OF RESPONSES

The survey responses show a marked concentration from Europe and North America, which together accounted for more than 80% of submissions with over 50% completion. European participation spanned Western, Southern, and Northern regions, while North American responses were mainly from the United States and Canada.

In Latin America, fewer responses were received, but complete submissions came from Chile, Argentina, and Mexico, demonstrating active professional engagement despite more limited institutional resources. Oceania was represented by Australia, contributing both complete and partial responses. Figure 7.2 and Appendix C.2 shows the number of responses completion per country.

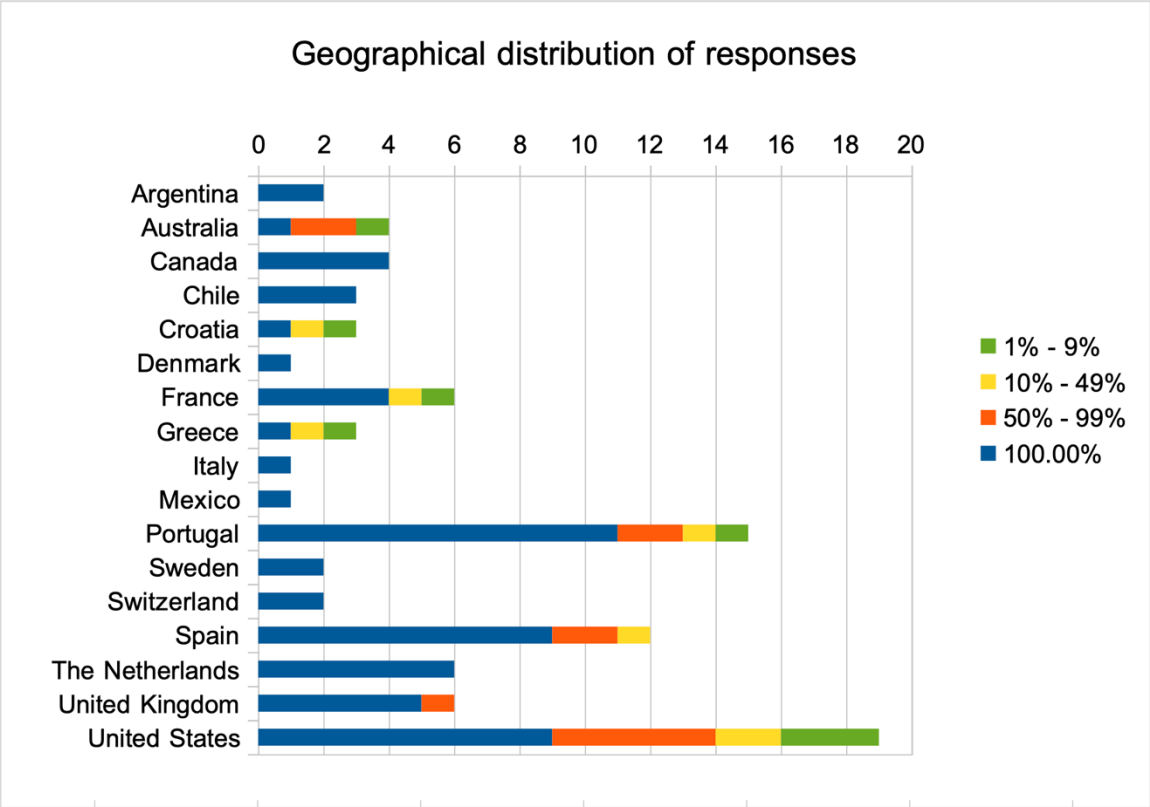


Fig. 7.2 –Total number of questionnaire responses by country, including the percentage of completion.

High participation from the United States, Portugal, Spain, and the Netherlands is notable. Italy, despite its recognised leadership in archaeological and Renaissance bronze studies, is underrepresented, probably owing to survey reach or institutional availability rather than low professional activity.

The Netherlands stands out both for its number of responses and for the role of the University of Amsterdam in training metal conservators, illustrating the influence of academic institutions on international participation.

Overall, the predominance of Europe and North America reflects the presence of well-developed conservation infrastructures, established academic networks, broader access to specialist training, and supportive cultural policies. High participation from Portugal, the

United States, and Spain may also relate to the prominence of bronze collections and monuments, as well as to specific conservation challenges in these countries.

The limited representation of other regions highlights the need to expand the geographic scope in future studies. Addressing barriers such as language, digital dissemination, and local relevance could help increase participation in underrepresented areas. It should also be noted that no countries from Africa or Asia were included in the distribution of the questionnaire, with the sample focusing primarily on Western contexts whose casting techniques are deeply rooted in European traditions. This situation parallels that described in Chapter 1, where the historical overview of bronze casting was largely confined to the European sphere. The study of these possible differences could be undertaken in future research, beyond the scope of the present thesis.

7.4 PROFESSIONAL PROFILE OF THE PARTICIPANTS

The institutional and professional profiles of respondents provide essential context for interpreting the data and for understanding the perspectives from which bronze conservation challenges are addressed.

Most responses came from museum staff (34), followed by conservation-restoration companies (22) and freelance conservator-restorers (21). Ten responses were from public institutions such as heritage agencies or government bodies, and two from art foundries, whose technical perspectives are particularly valuable given their more limited access to conservation specialists (Figure 7.3).

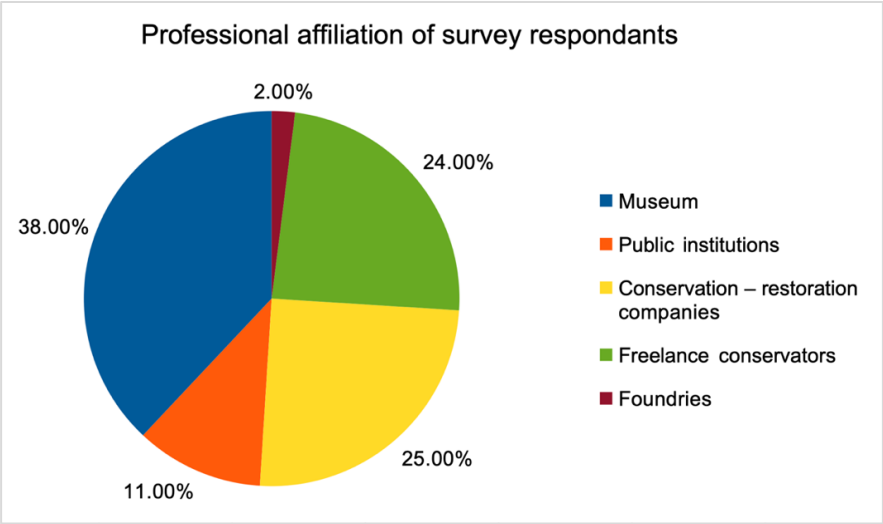


Fig. 7.3 - Participants' institutional affiliations, representative of the diversity of professional contexts involved in bronze sculpture conservation.

Experience levels show a predominance of highly experienced practitioners, many with over two decades in the field, alongside mid-career professionals and a smaller group of early-career respondents. This diversity, shown in Figure 7.4, reflects a wide range of professional experience.

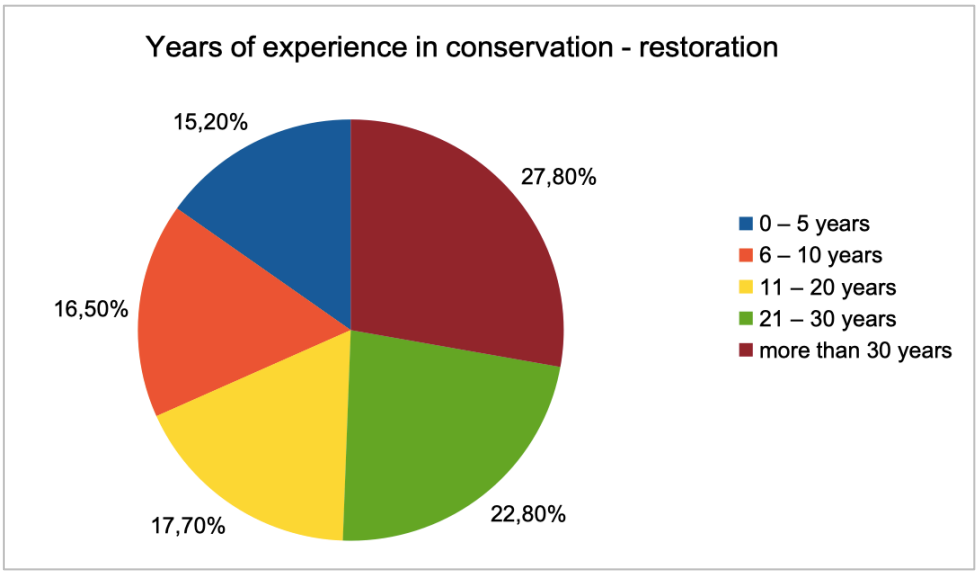


Fig. 7.4 - Distribution of respondents by years of experience in conservation–restoration, showing a predominance of highly experienced practitioners alongside mid- and early-career professionals.

Institutional capacity varied significantly. Large museums and national heritage centres often employed four or more metal conservators, with some reporting up to eight. Conversely, many smaller institutions operated with only one conservator, a situation especially common in local museums, small public bodies, and some research or educational centres. Independent studios and private companies typically had two or three conservators, while freelancers usually worked alone, sometimes collaborating with colleagues.

Museums account for the largest share of bronze conservation professionals, followed by private studios and companies, smaller public institutions, and freelancers. This heterogeneity influences both the scope and the continuity of interventions.

7.5 TYPES AND SETTINGS OF BRONZE SCULPTURES IN CONSERVATION

Survey responses show extensive experience with a wide variety of bronze sculpture formats. The most frequently treated are busts, small statuettes, and life-size sculptures, with monumental works also represented in many collections. This range illustrates the diversity of intervention contexts, from museum objects to outdoor public art.

Location is approximately evenly divided between indoor and outdoor works. Statuettes and busts are usually indoors, while life-size and monumental sculptures are most often outdoors, exposed to harsher environmental conditions. This distinction is crucial for analysing deterioration patterns and for planning treatments, as exposure strongly influences corrosion processes.

7.6 COMMON METAL AND SURFACE ALTERATIONS IN BRONZE SCULPTURES

7.6.1 Metal-related alterations

Responses identified recurring issues affecting the metallic core of bronze sculptures (Figure 7.5). The fracture or loss of fragments, often severe, results from material fatigue, accidental impacts, vandalism, or poor installation and handling. Deformation caused by impacts or falls, while not always compromising stability, can distort form and create internal stresses.

Many respondents also noted old or incompatible repairs, often undocumented, which have caused further damage due to non-reversible materials or invasive methods. These findings emphasise the importance of reviewing each piece's technical history before intervention.

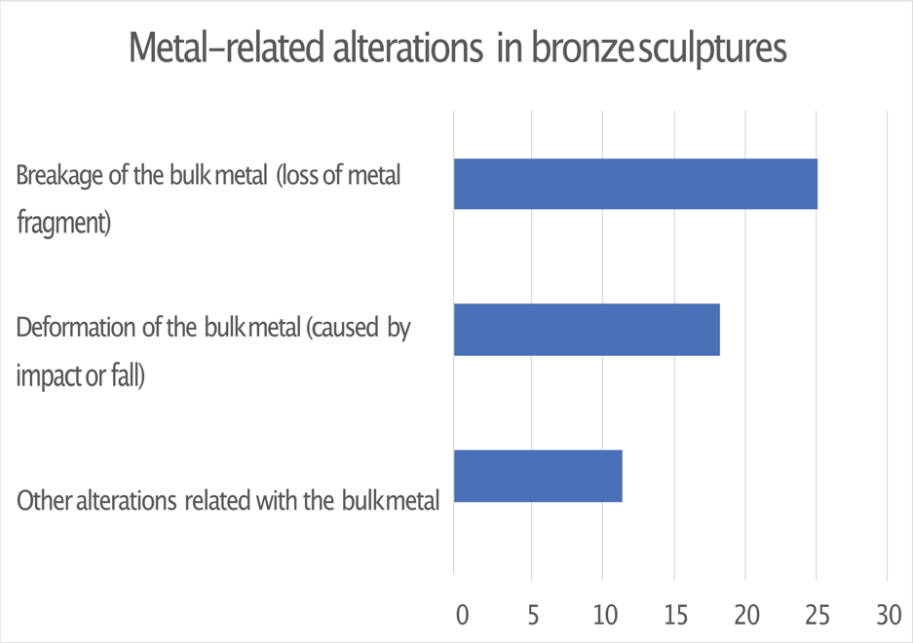


Fig. 7.5 - Metal-related alterations in bronze sculptures.

The fracture or loss of metal fragments is among the most frequently reported issues. These often represent severe structural damage and may require invasive treatments. Causes cited include material fatigue, accidental impacts, vandalism, and poor installation or handling conditions.

Metal deformation from impacts or falls is also common. Although in some cases it does not compromise structural stability, it distorts the sculpture's original form and can create internal stresses that weaken cohesion over time.

Many respondents highlighted the presence of old or incompatible repairs. These interventions, often undocumented, have sometimes introduced additional damage, particularly when non-reversible materials or mechanically invasive methods were used. Such cases underline the necessity of reviewing the technical history of each piece before intervention.

7.6.2 Surface-related alterations

A large share of reported issues affects the surface layers (Figure 7.6). The most common is harmful patina formation, particularly hydroxychlorides, arising from adverse environments, past incompatible treatments, or insufficient preventive care. Leaching is frequent on outdoor works, where runoff carries soluble corrosion products and leaves streaks or deposits; it is linked to prolonged rainfall, irrigation, or treated fountain water.

Graffiti, mainly in unprotected public spaces, reduces legibility and patina stability. Rough patinas occur through wax build-up, poor maintenance, or unchecked corrosion. Active corrosion and oxidation appear as stains, colour changes, or general surface degradation, especially in outdoor works lacking maintenance. Pollutants such as urine and bird droppings form crusts or stains that promote localised corrosion.

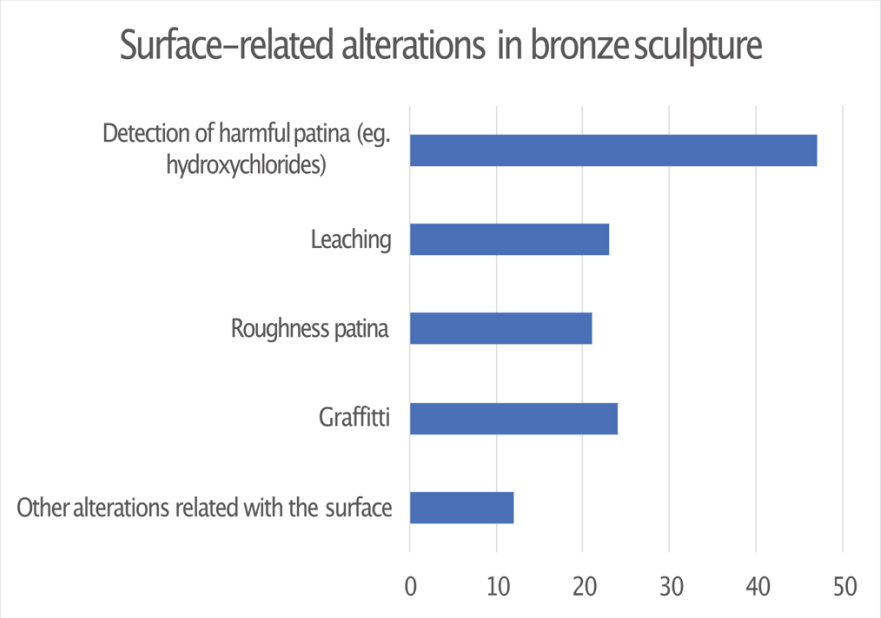


Fig. 7.6 - Surface-related alterations in bronze sculptures.

Other issues include residues from waxes, cleaning agents, or handling, which create opaque films or marks that diminish clarity. Past interventions with incompatible lacquers, excessive layers of wax or non-reversible artificial patinas have themselves become agents of deterioration, hindering new treatments and altering visual integrity.

7.7 ANALYTICAL TECHNIQUES REPORTED IN THE QUESTIONNAIRE RESPONSES

The questionnaire revealed a wide range of analytical methods used in bronze sculpture diagnosis (Figure 7.7). A detailed breakdown of responses by institution type is available in.

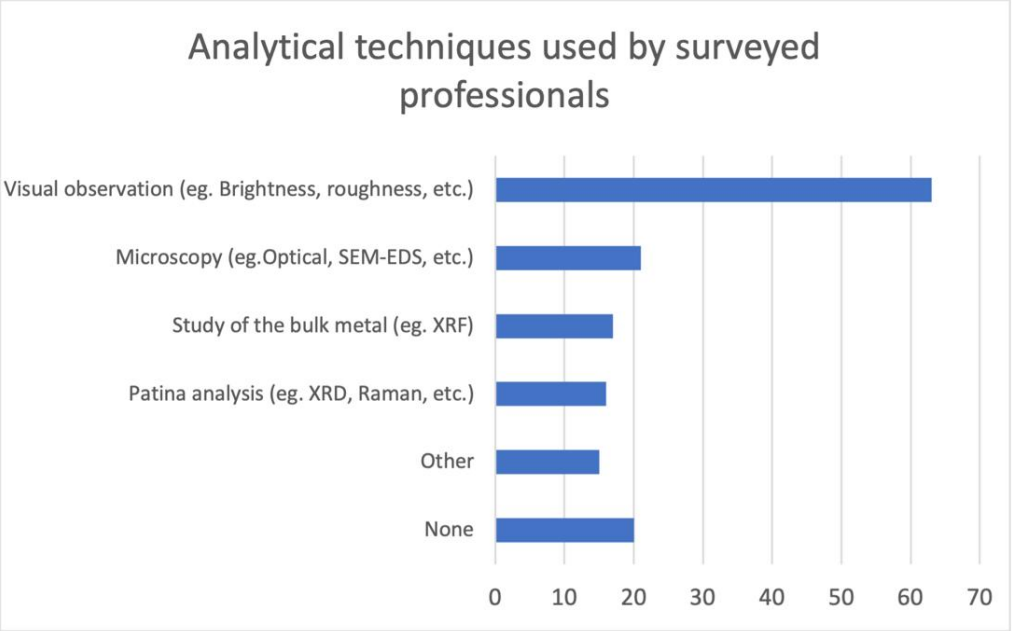


Fig. 7.7 - Distribution of analytical techniques employed by surveyed professionals in the conservation of bronze sculptures.

The most frequently cited method was visual (organoleptic) examination, used as a first step for visual and tactile assessment. This was particularly common in museums, which reported its use at nearly twice the rate of other institutions.

Microscopy techniques, including binocular magnification, optical microscopy (OM) and SEM-EDS, were used less frequently and mainly within museum contexts, allowing for the detailed observation of corrosion morphology, patina structures and surface deposits. However, the information provided in the questionnaire does not allow for clarification of the specific conditions under which these techniques were applied in the documented cases.

It should be noted that OM and SEM-EDS are considered invasive techniques, as they require the extraction of a small fragment of material. It can therefore be assumed that conservator-restorers who employed these methods were working with objects that showed a significant degree of metal degradation or, as in the case of the statue of King Afonso Henriques, studied in this research and discussed in Chapter 5, had areas with casting flaws

that were easily detachable, thus enabling sampling without compromising the integrity of the work.

Elemental metal analysis with XRF and patina analysis with XRD were also concentrated in museum contexts, with limited use elsewhere. When these four categories are considered together (organoleptic, microscopic, metal analysis and patina analysis), museums emerge as the most likely to apply them comprehensively. Some freelance conservators and companies reported using three of the four methods (Figure 7.8).

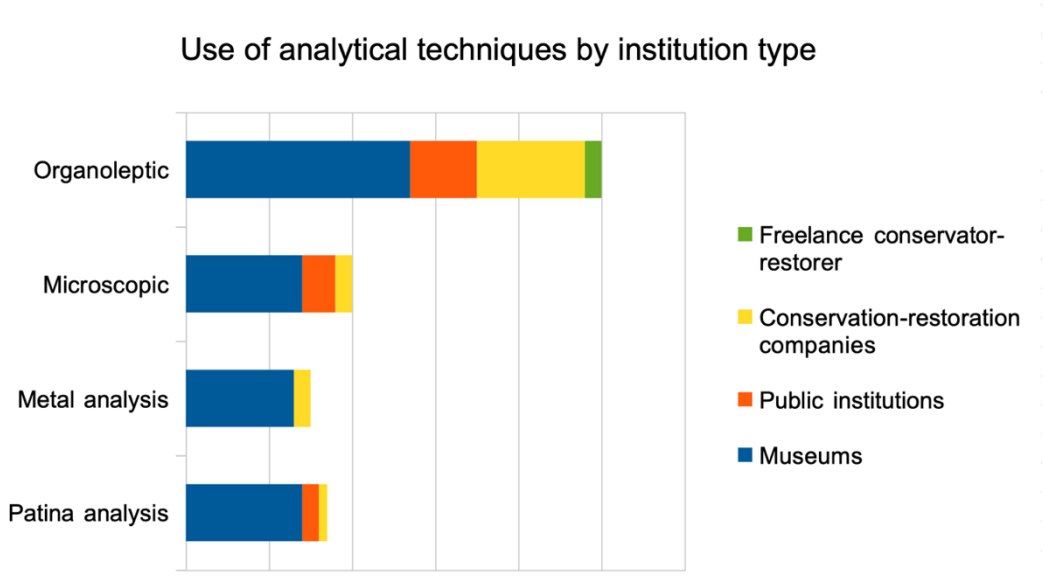


Fig.7.8 – Distribution of affirmative responses on the use of analytical techniques, by type of institution.

A few respondents reported using specialised techniques such as FTIR, GC-MS and NIR, mostly for identifying coatings and organic materials. Simple chemical spot tests were also noted, including chloride detection and solubility testing of coatings (e.g. graffiti, lacquers, resins). In some cases, analytical work was outsourced to external laboratories, particularly for large-scale or complex interventions. Historical documentation, treatment records, and photographic evidence were also valued as diagnostic tools.

A number of respondents (12.4%) indicated that they did not use analytical techniques, citing lack of access to equipment, trained staff, or funding, and the on-site nature of many interventions.

"Many times, in a site context, analysis is not possible due to lack of access, time, authorisations and available funds."

Budget constraints were a recurring reason for public institutions, freelancers and conservation companies:

"The client has no money for it, and I do not have access to the equipment."

Some stated they had only performed minor or preventive treatments, making advanced diagnostics unnecessary:

"Visual analysis based on experience is usually enough."

7.8 CONSERVATION INTERVENTIONS REPORTED IN THE QUESTIONNAIRE RESPONSES

7.8.1 Deformation treatments

Approaches to base metal deformation varied (Figure 7.9). Many museum professionals preferred not to intervene when stability and legibility were unaffected, prioritising preventive measures or minimal actions such as cleaning. Large or complex works were often outsourced to specialised companies.

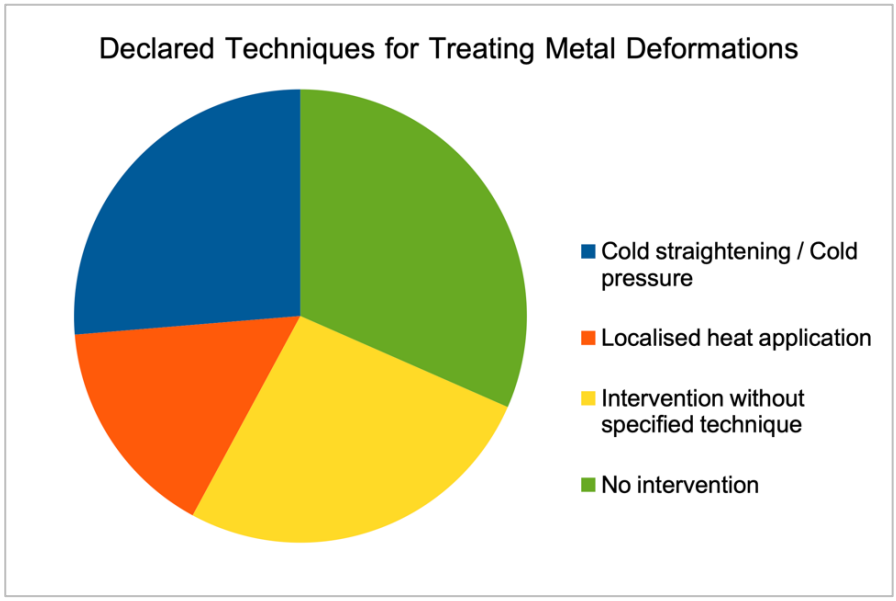


Fig. 7.9 - Declared techniques for treating deformations in bronze sculptures.

Conservation-restoration companies and independent conservators more often corrected deformations, using cold straightening or localised heat (heat guns, blowtorches), sometimes combined with cutting or chiselling, depending on severity and feasibility. No clear geographical pattern emerged; decisions appeared linked to institutional context, available resources, and underlying conservation philosophy.

Fractures were treated far more actively than deformations (Figure 7.10). Welding methods (TIG, MIG, soft soldering, brazing) were most frequently cited, often followed by weld bead chiselling, repatination and protective coatings. Copper-based filler alloys were occasionally used. These methods, requiring high technical skill in metalworking, were most common in conservation companies, but also present among freelancers and a few museums.

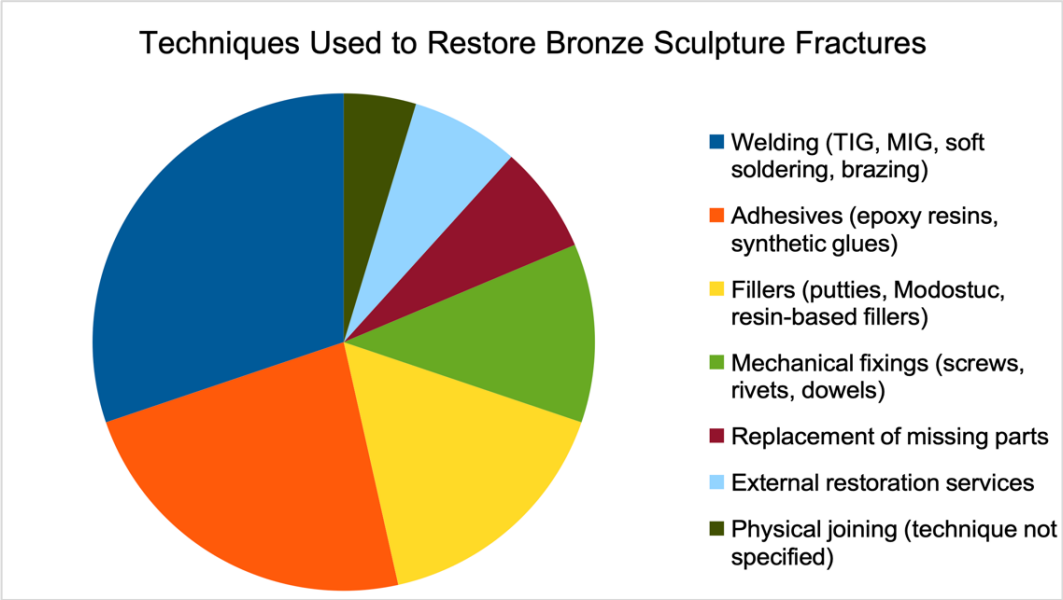


Fig. 7.10 - Distribution of restoration methods applied to fractures in bronze sculptures.

Epoxy resins, synthetic adhesives and fillers were also widely applied to reattach original fragments or fabricate replacements, with material choice guided by compatibility and colour-matching. Products mentioned included Araldite™ and Paraloid™. Mechanical systems (screws, dowels, rivets) were used mainly in smaller works or where welding was not viable, more often by museums and public institutions, sometimes combined with adhesives or fillers like Modostuc™ to ensure reversibility.

No respondents reported leaving fractures untreated, reflecting a consensus on the need for repair to ensure structural stability and visual integrity.

Although various techniques were mentioned, detailed accounts came from only about 30% of respondents, possibly due to absence of such needs, outsourcing of complex work, or limited experience. This highlights both uneven technical capacity and diverse approaches across institutions.

Reported tools included chisels, hammers, grinders, wooden wedges, and precision applicators (hake brushes, swabs, air blowers), enabling controlled treatment. Adhesives cited included epoxy and acrylic resins (Araldite™, Milliput™, Paraloid™ B-72/B-48N), valued for stability and, in some cases, reversibility. Epoxy putties and inert fillers were used for volumetric reintegration, with mineral pigments and selected coatings for colour integration.

7.9 REPORTED TECHNIQUES FOR THE REMOVAL OF SURFACE ALTERATIONS ON BRONZE SCULPTURES

The survey identified four main approaches for removing surface alterations from bronze sculptures: mechanical or abrasive cleaning, high-pressure water jetting, chemical cleaning, and laser ablation (Table 7.1).

Table 7.1 - Classification of mechanical cleaning techniques applied to bronze sculptures.

Category	Specific techniques mentioned
Manual methods	Fibreglass pencil, scalpel, micro-drill, bronze brushes, bronze wool.
Particle projection	Abrasion and micro-abrasion, sandblasting with corundum, glass beads, walnut shells, encapsulated rubber, dry ice blasting.

Mechanical or abrasive cleaning was the most frequently cited, particularly by museums and conservation-restoration companies, and less so by public institutions and freelancers. Techniques included fibreglass pencils, scalpels, micro-drills, bronze brushes, and bronze wool, as well as particle projection with corundum, glass beads, walnut shells, encapsulated rubber, and dry ice blasting.

High-pressure water jetting was widely reported across all institutional profiles and considered especially effective for removing soiling from outdoor sculptures. Both high-pressure jetting and mechanical methods are used globally, with no significant regional variation.

Chemical cleaning was also consistently mentioned, often in combination with other techniques to target specific corrosion products, coatings, or residues. Agents cited include chelating agents (EDTA, HEDTA, triammonium citrate), acids (citric, formic, oxalic), polar and non-polar solvents (acetone, ethanol, isopropanol, white spirit, toluene), as well as commercial paint strippers, gel-based graffiti removers, and surfactants like sodium lauryl sulphate and Triton X-100™ (Table 7.2). *Laser ablation* was mentioned only twice, likely due to its high cost, restricted availability, and applicability to highly specific and delicate contexts.

Table 7.2 - Surface cleaning materials mentioned by respondents.

Category	Materials
Chelating agents	EDTA, HEDTA, triammonium citrate (TAC), Rochelle salts
Acids	Citric acid, formic acid, oxalic acid
Polar and non-polar solvents	Acetone, ethanol, isopropanol, white spirit, toluene, isopropyl alcohol mixed with acetone

Paint removers and strippers	Paint strippers, methyl ethyl ketone (MEK), gel-based removers, commercial anti-graffiti products
Surfactants and detergents	Sodium lauryl sulphate (SLS), Triton X-100
Other cleaning agents	Ammonium bicarbonate, distilled water

7.10 REMOVAL OF CORROSION AND PATINA LAYERS

Patina removal, though a controversial aspect of bronze conservation, is accepted in specific contexts. To assess current practice, the questionnaire asked respondents to indicate the extent of patina removal applied in their treatments. Four main approaches emerged (Table 7.3).

Table 7.3 - Levels of patina removal reported by respondents.

Type of Removal	Responses (n)	Percentage (%)	Most Frequent Institutions
Until the metallic surface is visible	14	13.33%	Museums, Conservation-restoration companies, Sculpture foundries
Until the first layer of patina (natural or artificial) is visible	37	35.24%	Museums, Public institutions, Freelance conservators
Leaving some visible green patina	31	29.52%	Conservation-restoration companies, Museums, Freelance conservators
Other	23	21.9%	Museums, Freelance conservators, Public institutions

Complete removal to bare metal, including natural corrosion and artificial patinas, was chosen by 13.3% of respondents, mainly from museums, companies and art foundries. This approach was most common in the United States and reported occasionally in Europe, Chile and Australia.

The most frequent method (35.2%) was cleaning until a stable patina such as cuprite, tenorite or an artificial layer was exposed, primarily by museum and freelance professionals. It was common in Portugal, Spain and the United Kingdom, but less so in the United States.

Selective removal of harmful corrosion while retaining green patina was reported by 29.5%, with a broad geographical distribution.

In the “Other” category, many indicated they do not remove patina, citing its historical value or the application of preventive conservation only. Limited interventions included removing coatings, targeting chloride corrosion, or leaving stable layers untouched. Several noted that each case is evaluated individually, based on the condition and context of the sculpture.

7.11 REPATINATION PRACTICES IN BRONZE SCULPTURE CONSERVATION

Repatination remains a common practice in bronze conservation. Of the 66 respondents to this question, 43 (65.2%) reported using it, while 23 (34.8%) do not. Among those who do, hot patination was the most common technique (30.4%), followed by pigmented waxes (21.7%), cold patinas (19.6%), and acrylic paints (10.9%). Less frequent methods included Paraloid™ with pigments and electrochemical techniques (2.2% each). Around 13% said the choice depends on the sculpture’s characteristics and location. Results are summarised in Figure 7.11.

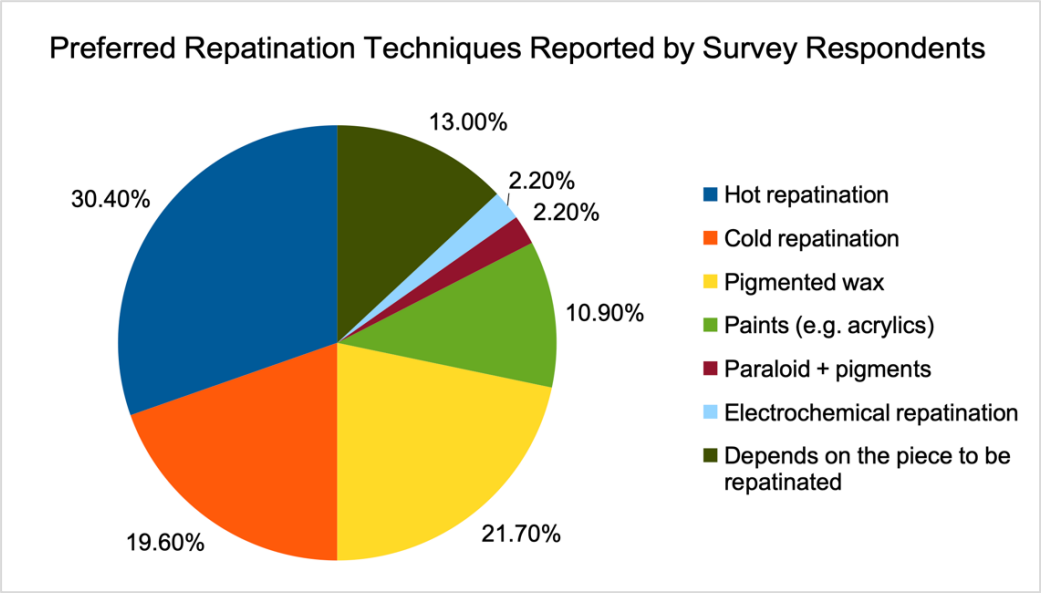


Fig. 7.11 - Techniques used for the repatination of bronze sculptures following patina removal.

Hot patinas are typically applied when the original layer has been severely lost. Cold patinas use commercially formulated patination fluids, while pigmented waxes or paints are generally applied locally, often in slightly lighter tones to distinguish the intervention from the original. Some sculptures originally painted rather than patinated were repainted, in some cases following the artist's guidance.

Those who do not repatinate cited respect for the sculpture's natural ageing, preservation of the original patina, or applying only limited colour reintegration when most of the surface remains intact. In archaeological collections, the patina is valued as part of the object's history and is left unaltered. Other reasons included the owner's aesthetic preferences or insufficient technical analysis to justify intervention.

Professionals using repatination techniques came from a wide range of institutions, including museums, public bodies, companies, and freelance practice, indicating broad acceptance across professional profiles. While approaches and materials vary, repatination is integrated into conservation practice when deemed appropriate.

Most responses came from Europe and North America, especially Portugal, France, the Netherlands, the UK, Switzerland, the US, and Canada, with additional responses from Australia, Argentina, and Chile.

7.12 PREVENTIVE CONSERVATION

Preventive conservation measures were reported for both indoor and outdoor bronze sculptures. Outdoor works require particular attention because they are constantly exposed to environmental agents such as rain, humidity, sunlight and urban pollutants, which accelerate deterioration. Indoor sculptures are generally better protected. Few respondents reported not applying preventive measures, especially for outdoor pieces. Most confirmed preventive actions in both contexts, although some museums focused only on outdoor works.

7.12.1 Indoor preventive conservation

The most common indoor measure is the application of microcrystalline wax as a protective coating (Figure 7.12). Wax is usually applied in several layers and sometimes used as the only protective product. Common brands mentioned include Cosmoloid™ H80, Reswax™ WH and Renaissance™ Wax. Some professionals mix wax with carnauba resin or pigments. More complex treatments often combine benzotriazole as a corrosion inhibitor with coatings such as Incralac™ (Incral 44™), Permalac™ or Paraloid™ B72, followed by wax. One respondent noted that benzotriazole is only used in sealed cases and when active corrosion is present, due to health risks in public settings.

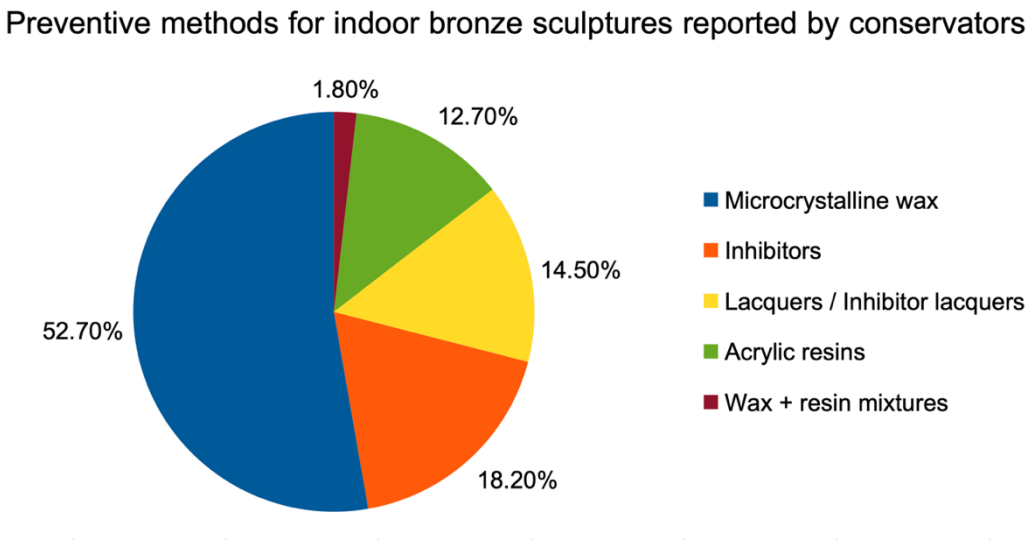


Fig. 7.12 – Distribution of preventive conservation methods applied to indoor bronze sculptures.

7.12.2 Outdoor preventive conservation

Outdoor treatments followed strategies similar to those used indoors, but required stronger and more durable protection (Figure 7.13). Microcrystalline wax was once again the most frequently reported coating, with Renaissance™ Wax and TeCero-Wax™ 3534F also commonly employed.

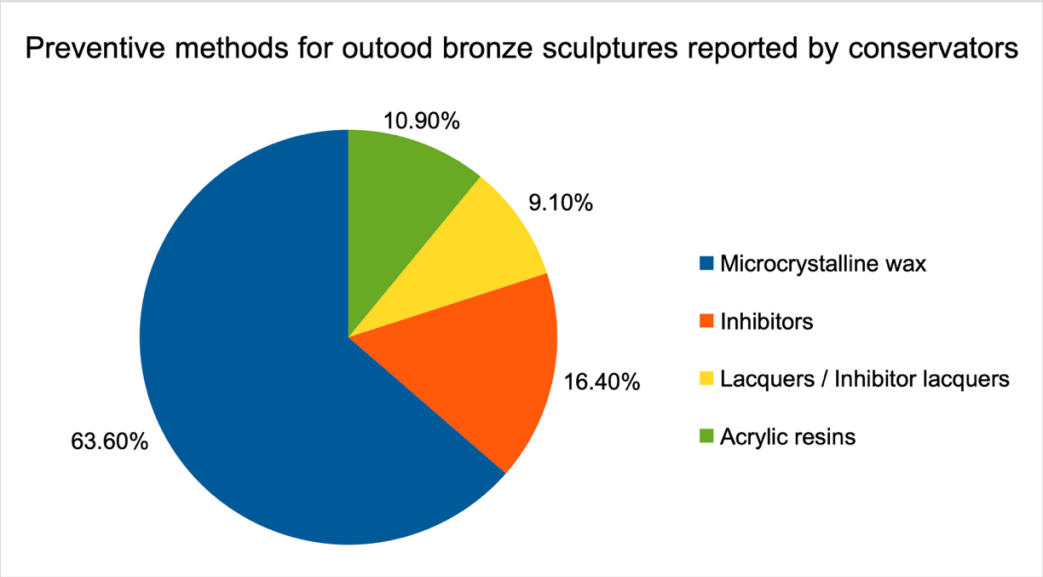


Fig. 7.13 – Distribution of preventive conservation methods applied to outdoor bronze sculptures.

Multi-step protocols were especially common outdoors and often included the use of benzotriazole, particularly in sculptures exposed to harsh climatic conditions. In these cases, benzotriazole was typically applied in combination with other protective coatings such as Incralac™, Incral 44™, and Paraloid™ formulations (B44, B64, B72). These were generally layered and finished with wax, which served as a sacrificial coating.

Outdoor conservation strategies thus mirrored those used indoors, but the scale, intensity, and environmental exposure demanded more robust protocols. Respondents highlighted that rewaxing cycles and the renewal of coatings were more frequent outdoors than indoors, owing to greater exposure to rainfall, pollution, and seasonal changes.

7.12.3 Additional maintenance measures

Beyond surface treatments, many institutions reported a broad range of complementary maintenance actions, reflecting a holistic preventive approach. These were grouped into four thematic categories summarised in Table 7.4. Such practices highlight a growing institutional commitment to long-term preventive care, often adapted to specific environmental or organisational contexts.

Table 7.4 – Complementary preventive maintenance actions reported by institutions.

Category	Practices reported by respondents
Routine cleaning and care	Dust removal, washing (with water, pH-neutral detergent or ethanol), redistribution of wax layers, removal of graffiti and bird droppings, patina polishing, storage cleaning
Environmental control	Corrosion checks, temperature and humidity monitoring, photographic documentation of corrosion, leaf removal, bird deterrent systems
Structural protection	Sealing holes and pores, drainage hole checks or creation, replacement of aged coatings, grass removal, installation of anti-theft anchors and protective perimeters
Training and awareness	Cleaning staff training, technical team education, advice to sculpture owners and gardeners, vandalism deterrence, use of gloves and appropriate storage/exhibition materials

7.12.4 Frequency and criteria

Maintenance frequency depends on location, condition, accessibility, available resources and risks such as vandalism. Indoor cleaning, especially dust removal, is carried out more regularly because it requires fewer resources. Outdoor maintenance is more structured: rewaxing is usually performed every 1–3 years, protective coatings are replaced every 3–5 years, and acrylic resins renewed about every 7 years. In highly exposed urban or coastal sites, interventions may be necessary every 4–5 months. Although an annual cycle is often considered ideal, budget and staffing constraints frequently extend intervals to 3–5 years.

Other factors influencing scheduling include the sculpture's museographic function (exhibition or loan), visible deterioration, and specific issues such as graffiti or biological deposits. Even when preventive care is not part of a formal contract, conservators often recommend regular inspections, weekly removal of biological residues and annual cleaning. Figure 7.14 summarises reported frequencies.

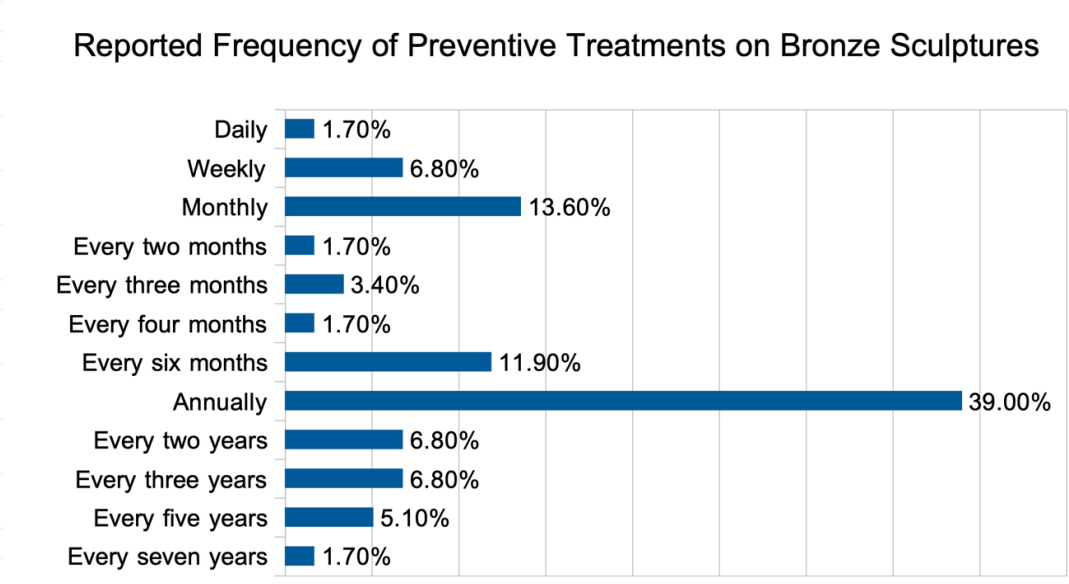


Fig. 7.14 - Reported frequencies of preventive conservation treatments on bronze sculptures. Short-term actions refer mainly to inspections and basic cleaning, while longer intervals (annual or more) correspond to complex interventions such as rewaxing or coating replacement.

7.13 SUSTAINABLE CONSERVATION

In recent years, sustainability has become increasingly important in cultural heritage conservation. This reflects growing awareness of the environmental impact of certain practices, health risks to practitioners, and the need to ensure the long-term stability of artworks. There is now a stronger push to reassess traditional materials and methods, favouring those that minimise chemical hazards, reduce waste, and make more efficient use of resources without compromising treatment effectiveness.

About 71% of respondents reported adopting environmentally responsible measures or actively seeking to reduce the environmental footprint of their work. While not all had formal protocols in place, there was a clear trend towards sustainable approaches. Common strategies included reducing the use of toxic solvents in favour of cleaning gels, dry ice, or certified green alternatives; reusing materials such as cloths, containers, and packaging; and ensuring hazardous waste was managed through disposal by specialised companies. Sustainability was also linked to minimal intervention and the preference for reversible or non-invasive treatments.

Some participants reported involvement in European initiatives such as *GreenArt* (www.greenart-project.eu), which focus on the development of sustainable conservation materials and methodologies. Although technical and financial barriers still limit the wider adoption of these practices, many professionals stressed the value of small-scale actions as practical and meaningful steps towards long-term change in the field.

7.14 KEY CHALLENGES IN THE CONTEMPORARY CONSERVATION OF BRONZE SCULPTURES

Building on the results presented in the previous section, this subsection critically examines the main challenges currently shaping the conservation of bronze sculptures. The aim is not merely to list problems, but to identify patterns and relationships that can guide improvements towards more coherent, sustainable, and technically sound practices. Responses to the questionnaire reveal that the difficulties extend beyond the inherent complexity of the material, also reflecting inequalities in access to technical diagnostics, diversity of criteria and methods, insufficient preventive planning, and only partial integration of sustainability principles in decision-making.

Although each of these challenges can be analysed separately, their interdependence is clear: the lack of technical diagnostics influences treatment choices; differences in criteria and resources affect the quality and consistency of interventions; and the absence of systematic preventive protocols increases the likelihood of resorting to more invasive procedures. The following analysis systematically addresses the main challenges identified, highlighting their technical, ethical, and environmental implications.

7.14.1 Recurrent Alterations and Technical Diagnosis

The most frequently reported alterations, such as fractures, deformations, unstable patinas, leachates, or residues from previous treatments, are well documented in specialised literature (Barclay et al., 2018; Scott, 2002; Strandberg, 1997; Weil et al., 1982). Their persistence cannot be attributed solely to the natural degradation of copper alloys; rather, it reflects structural shortcomings in long-term planning, continuity of maintenance, and the technical documentation of past interventions.

Particularly notable is the repeated mention of wax accumulations, lacquer deterioration, and the presence of urban contaminants or biological agents, especially in objects displayed outdoors. These conditions highlight the need to strengthen preventive conservation programmes through regular monitoring and protocols tailored to specific environmental and institutional contexts. Incorporating sustainability criteria at this diagnostic stage would also allow the selection of materials and methods that are less aggressive and have a lower environmental footprint.

7.14.2 Analytical Gaps and Unequal Access to Diagnostics

The use of analytical techniques reveals a marked disparity between types of institutions: museums account for the majority of positive responses regarding the use of technical diagnostics (such as microscopy and elemental analysis), whereas in other contexts their application is limited or non-existent. Factors such as lack of equipment, budgetary constraints, difficulties in accessing objects, or the perception of bronze as an "inherently durable" material reduce the priority given to these studies.

This situation encourages reliance on visual observations or professional experience, which, although valuable, cannot replace the capacity to assess complex processes such as active corrosion or the interaction of incompatible materials. In this regard, facilitating access to analytical methods for conservators and restorers who lack their own infrastructure constitutes a strategic priority, whether through inter-institutional cooperation programmes, equipment loan networks, or shared analytical services, thereby ensuring that decision-making is supported by reliable and comparable technical information.

The challenge is not only to provide access to equipment but also to develop interpretative skills to apply results critically and ethically. Sustainability, understood here as resource optimisation and the prevention of unnecessary treatments, directly benefits from more precise and accessible diagnostics.

7.14.3 Structural Interventions: Technical Diversity and Ethical Reflection

The analysis of structural interventions reveals a broad range of approaches, shaped by the type of institution and the resources available. Museums and public organisations tend to adopt conservative approaches, emphasising documentation and preventive maintenance, while independent professionals or specialised companies are more inclined to carry out direct, and occasionally more invasive, interventions when the stability or formal integrity of the artwork is at risk.

The techniques employed, ranging from epoxy or acrylic resins to welding and mechanical reinforcements, demonstrate technical expertise but also highlight disparities in access and decision-making criteria. In some cases, more complex interventions are outsourced to foundries, a practice that is not always feasible in every context.

Selecting an appropriate method requires balancing effectiveness, compatibility, reversibility, and environmental impact, considering both the immediate solution and its long-term behaviour. Establishing shared technical standards and fostering dialogue among custodians or owners of bronze sculptures, conservators-restorers, and other professionals in the artistic bronze sector, such as foundry workers, would encourage a more coherent and ethically grounded culture of intervention aligned with sustainability principles.

7.14.4 Surface Treatments: Cleaning and Informed Decision-Making

The removal of unstable patinas, deposits, or altered coatings is one of the most critical interventions due to its direct impact on the visible materiality. Responses reveal a wide range of methods, from manual mechanical techniques, valued for their control and adaptability, to particle blasting systems or laser ablation. While mechanical techniques

allow close supervision, they require a rigorous assessment of their possible cumulative effects.

The use of gels containing chelating agents, diluents, and surfactants has improved the precision of chemical treatments but demands a solid diagnosis and specialised training. It is notable that, in some cases of cleaning and removal, such as graffiti, some responses reported the use of products that are ineffective for this purpose. This highlights the need for better-informed selection and protocols adapted to the nature of each deposit.

More invasive methods, such as abrasive blasting, can compromise the integrity of the artwork if not applied under strict criteria. Emerging technologies like lasers, although promising, must be evaluated beyond their technological appeal, taking into account costs, risks, and actual benefits. Sustainability in this field involves prioritising techniques with lower environmental impact and toxicity, as well as limiting unnecessary interventions.

7.14.5 Repatination: Critical Decisions in Bronze Conservation

Repatination, understood as a strategy to restore aesthetic or interpretative values in bronze sculptures, is a well-established practice, although it remains subject to debate. While most professionals who responded positively to this question apply it under certain conditions, the answers reveal a remarkable diversity of techniques and motivations. This confirms that repatination is not a standardised procedure but rather a decision-making process influenced by material, institutional, and symbolic factors, where technical, historical, aesthetic, and ethical considerations converge.

The technical repertoire cited includes hot and cold patinas, pigmented waxes, commercial products, and even paint. Their application requires not only technical skill but also critical justification, as it can affect the perception of authenticity and the preservation of original features.

A significant number of professionals and institutions choose not to repatinate, either out of respect for natural ageing, to preserve part of the original patina, or due to lack of analytical support. This position aligns with principles of minimal intervention and the preservation of the material biography of the object, especially in archaeological or historical collections.

In some cases, the aesthetic preferences of owners or the instructions of artists influence the decision, creating tensions with conservation criteria. Therefore, repatination must be based on technically and ethically justified decisions, supported by historical documentation, analytical diagnosis, and clear conservation objectives. Rather than a default aesthetic solution, each case should be evaluated individually and critically, considering its long-term impact.

7.14.6 Prevention and Maintenance: From Intention to Systematisation

There is a general commitment to preventive conservation, especially for sculptures displayed outdoors. However, the way it is systematised varies depending on the technical and operational capacities of each institution. Common strategies include applying microcrystalline waxes or corrosion inhibitors, which are effective and easy to renew. Despite this, these treatments are often applied reactively and rely mainly on visual inspections.

One notable example is benzotriazole (BTA), the most widely used inhibitor. It is applied both on its own and mixed into protective layers with waxes or resins. Yet, the results show that its use is not always guided by a clear understanding of factors that affect its effectiveness, such as the application method or the type of alloy. These aspects will be explored in more detail in section 7.6. This case demonstrates how even widely recommended materials can lose their effectiveness if protocols are not properly followed.

Environmental monitoring and regular maintenance protocols are more common in institutions with their own collections. In contrast, service providers tend to limit their recommendations to the end of the intervention. Formalising maintenance plans with clear responsibilities, appropriate schedules, and sustainable criteria would promote more consistent and preventive management.

7.14.7 Sustainability: An Evolving Aspiration and Summary of Challenges

The responses reflect a generally positive attitude towards incorporating sustainability into conservation and restoration, demonstrating a growing awareness of the environmental, health, and material impacts of professional activity. However, this shift remains in its early stages. The actions reported in the questionnaire focus mainly on operational aspects, such as replacing solvents or recycling materials, rather than on a structural transformation of the technical frameworks that underpin treatments.

While these measures represent genuine progress, their implementation often depends on individual decisions rather than formalised institutional protocols, making sustainability more of a shared aspiration than a fully integrated criterion. Some responses, such as participation in collaborative projects like *GreenArt* (www.greenart-project.eu, accessed 14 July 2025), show an emerging interest in linking sustainability with technical effectiveness and ethical responsibility, although widespread adoption remains limited.

This situation provides a favourable context for advancing sustainable approaches that incorporate environmental criteria from the earliest planning stages. Integrating environmental indicators into treatment evaluation, exploring new material formulations, and promoting training that combines technical competence with ecological awareness are essential steps. Even small-scale actions can significantly contribute to a gradual transition towards more responsible practices aligned with the current challenges of conservation.

Overall, the challenges identified in this subsection reflect not only the technical complexity of bronze conservation but also the discipline's evolution in response to new ethical, environmental, and operational demands. Despite persistent inequalities in access to resources and fragmented practices, the professional commitment to critical reflection, ethical responsibility, and methodological development offers fertile ground for establishing a more coherent, collaborative, and sustainable conservation culture. This culture should be based on shared knowledge, specialised training, and decisions guided by technical rigour and the unique material history of each sculpture.

7.15 FINAL REMARKS ON CHAPTER 7

The survey results provide a comprehensive overview of contemporary practices in bronze sculpture conservation, reflecting both the technical diversity of the field and the uneven distribution of resources and expertise across institutions and regions. While the data confirm the persistence of recurrent alterations such as fractures, deformations, and unstable patinas, they also highlight the challenges posed by incompatible past treatments, limited preventive planning, and disparities in access to analytical tools.

The analysis shows that approaches to diagnosis and intervention remain heterogeneous, shaped by institutional capacities, conservation philosophies, and professional backgrounds. Preventive measures and repatination practices are widely employed but lack consistent protocols, while surface cleaning and coating treatments continue to raise concerns over effectiveness, reversibility, and environmental impact. Sustainability, though increasingly acknowledged, is still implemented mainly through small-scale operational adjustments rather than structural changes to conservation frameworks.

Overall, the findings underline the need for greater standardisation, improved access to diagnostics, and stronger integration of preventive and sustainability criteria. At the same time, they reflect a shared professional commitment to ethical responsibility and methodological development, offering a foundation for advancing towards more coherent, collaborative, and environmentally responsible practices in bronze conservation.

CHAPTER 8. CONSERVATION OF BRONZE SCULPTURES

8.1 INTRODUCTION

The conservation of bronze sculptures involves challenges that make it impossible to define universal or rigid protocols. Each work requires an individual approach, shaped by factors such as the composition of the alloy, its geographical setting, and above all the environmental conditions in which it is located. These include the proximity to sources of contamination, the distance from the sea, the level of human activity, or, by contrast, the presence of cleaner and less aggressive environments. As discussed in Chapter 6, these factors strongly influence the types of corrosion that develop and therefore the strategies most suitable for conservation. Even in processes that appear standard, such as cleaning or the application of protective coatings, these variables determine both the choice of methods and the degree of intervention.

One of the most common aspects of bronze sculpture conservation is the removal of corrosion products. This is far from a routine action: it requires clear criteria about how far the cleaning should go. Identifying the type of corrosion present on the surface is essential, since it is not always necessary to remove it completely or to apply a new patina afterwards.

In some cases, stable corrosion can be part of the historical and aesthetic value of the work. As noted in the 1882 quotation by journalist Manoel M. Rodrigues, reproduced in the introduction to Part III, patina can be seen as a visible mark of history, giving the sculpture dignity and reinforcing its historical character.

A striking example is the sculpture *Eva*, by the Italian artist Marcello Mascherini (1906-1983). After standing for decades in the gardens of the Hausbrandt family in Trieste, the piece was donated in 2011 to the Revoltella Museum in the same city. According to the museum's director, Susanna Gregorat, the institution's wish was to preserve the sculpture with its green corrosion films, just as it had been kept in the garden, thereby maintaining its evocative character (fig. 8.1). In her own words:

"mantenere lo stato di conservazione dell'opera così come si presentava, per il fascino che da questa promanava, quasi 'Eva' fosse una sorta di divinità silvestre" (S. Gregorat, personal communication, 6 June 2024).

"To maintain the state of conservation of the work as it appeared, for the fascination it emanated, as though 'Eva' were a kind of woodland divinity."



a b

Fig. 8.1 – Sculpture *Eva* by Marcello Mascherini. a) original location in the garden of the Hausbrandt family, Trieste. b) current location in the Revoltella Museum, Trieste. In the museum it retains the corrosion features acquired during its outdoor display. © Museo Revoltella.

This example shows how important it is to consider not only the nature of the corrosion film but also the environmental and museographic context in which the sculpture is preserved.

Fractures and breaks are also commonly encountered. Responses to the international questionnaire revealed a range of repair approaches, from the use of epoxy resins to metallurgical techniques such as welding.

In this area, the role of the metal conservator-restorer requires not only technical knowledge but also the ability to build collaborative links with responsible art foundries that understand the correct processes for bronze restoration. Access to such foundries is not always easy, but interdisciplinary cooperation is a vital part of the profession. For bronze sculptures, collaboration with founders and specialised technicians not only expands the range of possible treatments but also helps ensure conservation that respects the material and structural integrity of the works.

Overall, the conservation of bronze sculptures should be seen as a complex and contextual process, in which decisions combine technical, historical, aesthetic and ethical considerations. The diversity of situations and challenges makes it impossible to apply a single solution, underlining the need for flexible approaches based on sound diagnosis and interdisciplinary collaboration.

8.2 A BRIEF HISTORY OF METAL CONSERVATION IN EUROPE

Following the contextual framework outlined in the introduction to this chapter, it is important to recognise that current approaches to the conservation of bronze sculptures are rooted in the broader history of metal conservation. This history reflects the gradual transition from empirical craft-based practices to systematic scientific methods, particularly in Europe, where the discipline began to consolidate in the 19th century.

The origins of metal conservation lie in the need to stabilise and preserve archaeologically significant artefacts. Since Roman times, this work was undertaken by highly skilled craftsmen who specialised in the treatment of specific metals (Macarrón, 2021). This artisanal approach remained predominant until the 19th century, when a significant shift towards more scientific and systematic conservation methods began (Gilberg, 1987).

This methodological transformation was driven by advances in the understanding of metal degradation processes, as well as by the development of more sophisticated techniques and materials for stabilisation. Researchers and conservators started to apply methods based on chemical, physical, and metallurgical analysis, which enabled more effective and durable conservation of metal objects (Gilberg, 1987).

The first experiments in the conservation of archaeological metals, initially focused on iron objects, were undertaken in Norway and Denmark throughout the 19th century. These practices included the removal of chloride ions through immersion or washing in substances such as wax and boiled linseed oil, sulphuric acid and glycerine, as well as hot and cold distilled water baths and protection with paraffin, among other methods (Micheli, 2015; Weidling, 2023).

A notable contribution in the Scandinavian context was the publication of *Antiquités en fer et en bronze. Leur transformation et leur conservation*, written by Gustav Rosenberg in 1917, at the time head of the Conservation Department at the National Museum of Denmark.

During the 20th century, the removal of natural patina through electrolytic methods became widely popular. First refined in Scandinavia and Germany, these procedures spread across Europe but were ultimately abandoned towards the end of the century (Micheli, 2015).

In the 19th century, Germany became a key centre for scientific advances in conservation. Otto Olshausen, founder of the Conservation Laboratory at the Königliches Museum in Berlin, and his assistant Friedrich Rathgen marked a decisive phase in the field. In 1898, Rathgen published *Die Konservierung von Altertumsfunden* (*The Conservation of Antiquities*), a work focused specifically on archaeological metallic materials. As the first

director of the museum's Chemistry Laboratory (1888–1927), he introduced a methodology based on the analysis of corrosion causes and the development of alternatives for preserving cultural heritage (Gilberg, 1987).

Parallel to these European developments, the Metropolitan Museum of Art in New York also initiated pioneering projects. From the 1920s onwards, the arrival of large quantities of metal objects from archaeological excavations, particularly in Egypt, prompted the search for appropriate stabilisation methods. The institution collaborated with scientists such as Colin G. Fink, whose electrochemical techniques for treating archaeological bronzes were widely adopted, although later criticised for irreversibly altering the original appearance of surfaces.

In 1932, the museum took a decisive step by appointing Arthur H. Kopp as its first resident scientist. Kopp continued to investigate Fink's electrochemical methods but also broadened the museum's approach by integrating systematic study of metal objects from both analytical and conservation perspectives (Becker & Shorsch, 2010).

According to Becker and Schorsch, by the late 1940s, if not earlier, specific chemical formulations were in use at The Cloisters, the MET's medieval branch, for the conservation of metals. Silver was treated with a solution of ammonia and Gorham silver polish, followed by Randolph silver lacquer, a coating similar to Zaponlack as recommended by Fink. For copper alloys, a mixture of vinegar and salt was used, known as "Mr Rorimer's formula." These coatings aimed to prevent tarnishing and stabilise surfaces, combining empirical knowledge with the technical products available at the time.

Between 1940 and 1960, the MET began to incorporate scientific tools into the conservation of metal objects. A key development was the acquisition, in 1968, of an X-ray system powerful enough to analyse metal sculptures, allowing internal structures to be examined without direct intervention. Although the museum did not yet have dedicated scientific staff, these practices laid the groundwork for a more rigorous analytical approach, which would be consolidated from 1970 onwards with the appointment of a research chemist (Schorsch, 2020).

One of the most influential figures in 20th-century metal conservation was Harold Plenderleith. Educated at the universities of St Andrews and Dundee, he joined the British Museum's laboratory in 1924 and soon rose to lead its scientific team (Oddy, 2011).

In his book *Conservation of Antiques and Works of Art* (1956), Plenderleith devoted a chapter to metals, providing a systematic analysis of the properties of metallic objects and their behaviour in the presence of deterioration agents. The text addresses corrosion mechanisms, appropriate cleaning strategies for different metals, and the criteria for selecting stabilisation and protection treatments. Published at an early stage in the scientific development of metal conservation, the work helped to establish a methodological foundation that has had a lasting influence on professional practice.

Plenderleith also played a prominent role in training professionals, both through formal teaching and active participation in international technical forums. He was invited by museums and institutions across Europe to share insights on emerging conservation standards and methodologies.

One such occasion took place on 19 April 1956 at the MNSR in Porto, where he delivered a lecture to Portuguese museum professionals. His presentation addressed the challenges faced by artworks in wartime contexts, focusing on the material, logistical, and institutional risks associated with heritage protection during armed conflict (Couto, 1956). The lecture attracted considerable interest, and many directors and conservators requested copies. However, it was distributed only in limited numbers and never formally published, though it contributed to professional debate and reinforced Plenderleith's authority within the Portuguese conservation community.

Closely linked to Plenderleith's institutional influence at the British Museum, Robert M. Organ emerged as a key figure of the following generation. He joined the museum in 1951 and played a central role in applying chemical principles to the restoration of ancient bronzes.

In his article *Aspects of Bronze Patina and Its Treatment* (1963), Organ proposed a stratified model of corrosion in which compounds such as cuprous chloride (CuCl), cuprous oxide, and basic copper carbonate formed successively from the metallic core outwards. He emphasised the highly reactive nature of CuCl and its role in the progression of "bronze disease."

During the 1960s, Organ applied sodium sesquicarbonate treatments to stabilise a significant proportion of the bronze antiquities at the British Museum (Organ, 1968). He also highlighted the importance of identifying hidden original surfaces through radiography before any physical intervention. He proposed stabilisation strategies based on the removal, chemical conversion, or isolation of CuCl, and stressed the necessity of maintaining relative humidity below 40% to prevent active corrosion. His work consolidated a rigorous scientific approach that provided practical continuity to the methodological foundations laid by Plenderleith.

In the same historical context, Jorge de Alarcão and Adília M. de Alarcão carried out important research in Portugal on archaeological bronze objects preserved at the Museu Monográfico de Conímbriga. The outcome of this work was the publication of *A Conservação de Antiguidades de Bronze* (1965), a short text of considerable scientific and technical value. It provides information on the composition of archaeological bronze and describes the physical and chemical structure of corrosion products observed on objects.

The book is also notable for addressing the identification of corrosion processes without the aid of modern analytical techniques, relying instead on careful macroscopic observation and comparative reasoning. It includes a section on corrosion removal and on the conservation practices of the time, some of which are still in use today. Taken as a whole, this study represents a key precedent in the conservation of metals in Portugal and an important testimony to the development of conservation criteria and practices in Europe during the 1960s (Alarcão & Alarção, 1965).

At present, several studies have been conducted in Portugal focusing on the composition of monumental sculptures and on the corrosion products generated through their interaction

with the environment. These investigations have been carried out both by private enterprises and by public institutions, most notably the Laboratório Nacional de Engenharia Civil (LNEC) and the HERCULES Laboratory at the University of Évora, whose work has been discussed in Chapter 4 (Fontinha & Salta, 1996a, 1996b, 1996c; Salta & Fontinha, 1998a, 1998b, 1998c; Pinheiro, 2025). In both cases, the use of modern equipment has enabled the achievement of more accurate and reliable results, with the HERCULES Laboratory being responsible for the analyses that constitute the scientific basis of this thesis. The knowledge derived from these investigations has not only expanded the corpus of research on metals, but has also shed light on the state of conservation of heritage works of great significance in diverse geographical and environmental contexts.

This brief overview shows how metal conservation gradually evolved from empirical treatments to the establishment of scientific standards that remain influential today. The work of figures such as Rathgen, Plenderleith, and Organ helped to establish methodological foundations that continue to guide professional practice. From this point onwards, the study and treatment of corrosion in bronzes developed at an increasingly rapid pace, driven by advances in analytical science, by a stronger focus on preventive measures, and by the introduction of new products and materials, many originating in industry and medicine, which were subsequently adapted for use in conservation.

8.3 THE ROLE OF ANALYTICAL METHODS IN BRONZE CONSERVATION

Following the discussion in section 8.1, where the impossibility of universal protocols and the historical development of metal conservation were highlighted, this section focuses on the role of analytical methods as the foundation of decision-making in bronze conservation. Understanding the conservation state of bronze artefacts requires more than visual inspection or professional experience. Given the complexity and potential instability of these alloys,

particularly in outdoor or historical contexts, technical analysis plays a key role in guiding responsible and well-founded interventions. Without reliable diagnostic information, treatments risk being inadequate, overly aggressive, or incompatible with the object's material history.

Material analysis should not be regarded as optional, but rather as a fundamental component of ethical and effective conservation. In line with this premise, and building on earlier discussion in the chapter, analytical tools help to detect corrosion processes, identify previous treatments, understand material composition, and support treatment selection. At the same time, there are persistent limitations in access to, and training for, the use and interpretation of these techniques, as highlighted by the Bronze Conservation Survey.

The focus on scientific analysis points to a broader challenge: ensuring decisions are based on clear evidence, critically interpreted and aligned with the material and historical context of each object. As Caple (2000) observes, the value of analytical data lies not only in its accuracy but also in the conservator's ability to interpret and apply it critically. This integrated perspective is not new. Artioli (2010) warns that the lack of interdisciplinary training and the divide between sciences and humanities limit the effective use of analytical tools in heritage conservation. Furthermore, research, often framed within short-term projects, rarely becomes fully integrated into professional practice. Overcoming these limitations requires stable collaboration between researchers, analysts, and conservators-restorers so that technical information supports responsible and well-informed decisions (Kabbani, 1997).

Bronzes exhibit remarkable compositional diversity, resulting from technical decisions made during manufacture and from subsequent intentional or accidental modifications. Alloys with varying proportions of copper, tin, lead, or zinc behave differently when exposed to moisture, chlorides, contaminants, and temperature fluctuations, affecting their long-term stability. In some cases, however, the actual composition of the alloys is not even known, which further complicates the definition of appropriate conservation strategies. This complexity is increased by the accumulated effects of previous cleaning, stabilisation, or

aesthetic interventions, which may alter surface chemistry and microstructure. Such realities discourage generalisations and reinforce the need for case-specific material investigation capable of distinguishing active from benign corrosion, diagnosing residues from prior interventions, and identifying potentially unstable compounds while preventive action is still feasible.

A particularly illustrative example of this approach can be found in the reports produced by the National Laboratory for Civil Engineering (LNEC) in Portugal during the late 20th century (R. Fontinha & Salta, 1996a, 1996b, 1996c; Salta & Fontinha, 1998a, 1998b, 1998c). These studies involved exhaustive scientific examinations of the alloy composition and patinas of major bronze sculptures in Lisbon and Porto. Their results provided the basis for recommending whether or not conservation-restoration interventions should be carried out, demonstrating how rigorous analysis can directly inform responsible decision-making at an institutional level.

The analyses carried out in this research, presented in Chapters 4 and 5, also illustrate this complexity. Applied to artworks spanning different periods and exposed to diverse environmental conditions, these results provide essential knowledge to assess risks, select appropriate treatments, and plan sustainable long-term strategies.

From a conservation-restoration perspective, the key is not only to obtain results but to interpret them correctly and integrate them into diagnosis and decision-making (Leona et al., 2021). Professional observation and experience can and should be complemented by analytical techniques such as microscopy, XRF, XRD, or metallographic analysis. These methods enable a deeper understanding of the object's condition and can confirm or refine initial hypotheses. The aim is not to replace professional judgement with instrumentation but to reinforce it by clarifying which alterations are materially present, which are active, and the foreseeable consequences of a given intervention.

Alongside conventional laboratory techniques, accessible and innovative tools can also enhance diagnostic capacity where resources are limited. The online platform MiCorr (www.micorr.org), developed by Haute École Arc Conservation-Restauration in Neuchâtel,

allows visual identification of alloys and corrosion products through comparison with a reference database. Similarly, the low-cost software DiscoveryMat offers a portable electrochemical tool for preliminary alloy identification by monitoring corrosion potential in different solutions (Haute École Arc Ingénierie, 2025). Work with DiscoveryMat was conducted within the framework of a Short-Term Scientific Mission of the Endless Metal project (Appendix D.1), with direct training provided by the Endless Metal team during specialised workshops in Neuchâtel and Porto (General-Toro, 2023).

Although these methodologies are already applicable in practice, they are still under development, and their reference libraries continue to expand. Their integration must therefore be accompanied by cautious interpretation and clear documentation. To promote accurate identification of materials and processes, a proportional diagnostic sequence is proposed. It begins with observation and documentary review, continues with non-invasive or minimally invasive tests such as microscopy or halide ion detection, and only in cases of uncertainty or risk does it move towards selective analytical confirmation. The final decision must always remain aligned with conservation objectives and with the medium- to long-term maintenance capacity of the work (Clark, 2013).

The incorporation of lower-cost tools does not replace laboratory analysis, but it can significantly complement it, especially in the initial diagnostic phase or in projects with limited resources. Integrating such approaches into practice fosters a professional culture that is both critical and evidence-based, where decisions depend not only on intuition or experience but also on data rigorously interpreted.

In conclusion, analytical methods establish the foundation of responsible bronze conservation. They enable precise diagnosis, guide proportional intervention, and connect observation with scientific evidence. From this basis, the next section will examine how conservation techniques themselves have developed in recent decades, increasingly shaped by diagnostic advances and by the introduction of new products and materials into professional practice.

8.4 CONSERVATION OF BRONZE SCULPTURES: CONTEMPORARY METHODS

Building on the historical overview (section 8.2) and the role of analytical methods in guiding decisions (section 8.3), this section examines the range of contemporary approaches currently used in the conservation of bronze sculptures. These methods reflect the principles of conservation-restoration but must always be adapted to the specific characteristics of each object. The choice of treatment depends on factors such as alloy composition, the presence or absence of patinas, environmental exposure, and the record of previous interventions.

Rather than applying fixed or universal protocols, conservators must work within a flexible framework, balancing effectiveness, minimal intervention, and respect for the object's material history. In practice, this involves a combination of cleaning strategies, corrosion stabilisation, protective coatings, and maintenance regimes, each carefully adjusted to the condition and significance of the sculpture.

The following subsections provide an overview of the main methods reported in both the literature and the Bronze Conservation Survey, focusing on their effectiveness, limitations, and ongoing debates in professional practice.

8.4.1 Surface Cleaning as a Conservation Strategy

Surface cleaning is typically the first step in both indoor and outdoor conservation and was identified as the most frequently performed intervention by respondents. Although often regarded as a simple task, it plays a vital role in preventive conservation. It limits the accumulation of dust and pollutants, helps stabilise the surface condition, and reduces the need for more invasive treatments in the future. When carried out properly, it also supports the preservation of original coatings and slows down deterioration.

The cleaning methods vary depending on the size of the sculpture, its accessibility, and its location. For indoor objects, the most common tools include clean cloths, soft brushes, and vacuum cleaners, mainly used to remove surface dust. While dust may appear harmless, in environments without adequate control of temperature and relative humidity it can contribute to localised corrosion, especially when it contains hygroscopic or organic particles.
Outdoor sculptures are exposed to harsher and more variable conditions, which makes regular cleaning essential. Copper alloys such as bronze are particularly sensitive to moisture, especially when it contains chlorine. For this reason, rinsing with water is only appropriate when the surface has been previously protected with synthetic resins or microcrystalline wax, and only as part of a structured preventive maintenance plan with clearly defined procedures and intervals.

8.4.2 Mechanical cleaning methods in bronze conservation: effectiveness, control and risks

Mechanical cleaning is a widely accepted technique in the conservation of bronze sculptures, valued for its localised action and its apparent chemical neutrality, since it does not rely on solvents. It is routinely used for the removal of corrosion products as well as stains from natural causes, such as bird droppings, or from acts of vandalism, such as graffiti. This approach is especially suited to surfaces affected by strongly adhered deposits or resistant crusts, where less invasive techniques are ineffective.

Among the most used manual methods are scalpels, micromotors, metal brushes, fibreglass pencils, and bronze wool. These tools allow precise work on irregular surfaces and are particularly useful for small or medium-sized objects, as well as for interventions aimed at preserving artificial or historic patinas. Direct control of the tool enables gradual intervention, although the technique’s effectiveness depends heavily on the restorer's skill and sensitivity, which are crucial to avoid irreversible damage.

However, this apparent neutrality does not imply harmlessness. Any mechanical action entails a potential risk of abrasion or loss of original material, even with seemingly non-invasive tools. No technique is entirely safe, and its application must be guided by rigorous technical and ethical judgement, supported by a thorough understanding of the object's material history.

From an operational standpoint, manual cleaning demands considerable time and expertise. For this reason, in monumental sculptures or contexts with limited resources, more powerful methods are often employed.

Among these, assisted projection systems are notable, particularly when treating objects with encrusted corrosion products (e.g. black crusts) or graffiti. The most common abrasive methods include the projection of glass microspheres, walnut shells, and silica sand, applied using compressed air or pressurised water. As highlighted by Robbiola et al. (1993), compressed air abrasion allows precise modulation of pressure, abrasive type, and nozzle geometry, making it adaptable to the scale of the work or the type of deposit to be removed.

One prominent projection method in metal conservation is the use of dry ice, through the projection of ultra-cooled air or cryogenic CO_2. It is considered a sustainable technique because it reduces working time and minimises exposure to toxic substances. The method combines thermal shock, kinetic energy, and sublimation of the projected material, gradually removing corrosion and coatings without damaging the substrate. However, it is only effective on coatings present on the surface and not suitable for deposits that have penetrated the metal's porosity (Máša et al., 2021; van der Molen et al., 2011; Vega-Bosch et al., 2024).

In parallel, non-abrasive methods have also been developed, such as hot deionised water steam, applied at temperatures below 80 °C. This technique removes grease, dust, and salts without abrasion or chemical residues, but requires strict control of pressure, temperature, and distance. Localised testing is essential to avoid altering sensitive surfaces such as gilding or unstable patinas (Plé & Schröter, 2020). As with other wet methods, deionised water must always be used to avoid introducing soluble salts.

Regardless of the technique employed, method selection must be based on thorough technical diagnosis, including surface condition, identification of previous treatments, detection of existing coatings, and the choice of the least invasive procedure. In this context, institutional protocols such as that of the U.S. General Services Administration (GSA) *(2024)* are particularly relevant. This protocol establishes an intervention sequence based on the principle of minimum aggressiveness, beginning with dry brushing using natural-bristle brushes (with protected ferrules to avoid contact between metal and sculpture), followed by non-ionic detergents and rinsing with deionised water. In justified cases, soft abrasives such as walnut shell or CO_2 may be authorised, always under controlled conditions.

All procedures must be preceded by localised testing, using wide-angle nozzles (minimum 25°) and maintaining safe distances (at least 30 cm) to prevent overcleaning or damage. The consolidation of these standards builds on earlier protocols such as those of the U.S. National Park Service (1989), which recommended moderate-pressure hot water and soft abrasives, while explicitly discouraging the reuse of abrasive media due to the risk of cross-contamination. Similarly, the War Memorials Trust (2017) in the United Kingdom promotes gradual interventions, where abrasive or chemical techniques must be exceptional, justified, and always preceded by controlled tests.

In the museum field, institutions such as the Henry Ford – Benson Ford Research Center have developed guidelines for the cleaning of indoor or small-format sculptures, prioritising gentle and controlled intervention (Deck, 2020). These recommendations include the use of natural-bristle brushes and bamboo sticks for difficult-to-access areas, as well as diluted solutions of approved products in deionised water or mineral solvents, depending on the type of dirt present.

When surface dirt contains a high proportion of greasy compounds, the use of non-ionic detergents diluted in deionised water is recommended. These surfactants effectively solubilise and remove residues without introducing reactive ions or leaving residual compounds (Deck, 2020).

For calcareous encrustations or resistant deposits, soft abrasive pastes made of micronised calcium carbonate mixed with ethanol and water are recommended. These allow delicate mechanical cleaning without damaging stable patinas. On objects with heavier oxidations, occasional use of commercial polishes with low ammoniacal content may be considered, always after localised testing and with strict removal of residues using solvents such as white spirit (Deck, 2020).

Even carefully adjusted methods carry inherent risks. Sandblasting, for instance, can remove artificial patinas and expose bare metal, which is why it should never exceed 1.5 atmospheres of pressure (Bruni et al., 2019; Heuman, 1992). Moreover, its effectiveness against complex alterations such as black crusts is limited.

8.4.3 Use of laser in bronze

Among the most recent techniques, laser ablation has emerged as a selective and effective method for removing corrosion layers from archaeological, historical, and monumental bronzes. It is generally classified as a non-abrasive, contactless cleaning technique, in which deposits are removed through the physical action of laser radiation pulses, without chemical agents. This optical–thermal mechanism enables highly controlled cleaning, helping to preserve surface details and avoid mechanical abrasion.

One of the most critical parameters for safe and effective cleaning is the pulse duration, understood as the speed at which the laser delivers small bursts of energy. The shorter the pulse, the greater the control overheat penetration into the metal, and therefore the lower the risk of thermal damage.

Siano et al. (2003) demonstrated that short pulses in the nanosecond range (30–100 ns) can remove surface deposits while preserving original layers, provided the fluence is kept below

the damage threshold. These pulses are particularly suitable for fragile archaeological metals, as they reduce the risk of melting or detachment of material.

In contrast, Sansonetti et al. (2015) documented the use of longer pulses in the microsecond range (20–150 μs) for cleaning outdoor bronzes covered with calcareous and sulphated crusts or aged oleoresinous coatings. These longer pulses allow progressive removal of more resistant deposits while keeping heat input under control.

In practice, both approaches share the same principle: adjusting pulse duration to the type of deposit and surface fragility in order to achieve cleaning without compromising the object's integrity.

Studies on real artefacts confirm that, when properly calibrated, laser cleaning can reduce thick, stratified corrosion layers while preserving the underlying cuprous oxide structure (Di Francia et al., 2022). However, Sansonetti et al. (2015) observed slight colour variations and changes in surface gloss in some cases, attributable to localised thermal effects. Such alterations add to other known risks, including the formation of iridescent patinas or films that are difficult to remove.

Some interventions, such as the cleaning of Ghiberti's signature on the Florence Baptistery Doors, have shown that laser ablation may leave residual layers, revealing the limits of process control (Basilissi et al., 2022). Conversely, other applications, like the cleaning of the *Storie di Noé* panel from the same Baptistery, have demonstrated the full potential of laser cleaning when parameters are carefully tailored to the object, successfully removing deposits while preserving texture, patina, and stable cuprite areas (Siano et al., 2003).

Despite its advantages, laser technology requires high investment, precise calibration, and skilled operators. The process can also release harmful particles, such as metal oxides or chlorides, which demand extraction systems and strict personal protection measures.

In summary, the effectiveness and safety of laser cleaning depend on extremely precise calibration, adapted not only to the metal and corrosion type but also to the object's material

history and conservation state. Without this adaptation, risks may outweigh benefits, compromising both stability and aesthetic perception.

Although laser ablation is a powerful tool, it must always be assessed critically. Prior characterisation of corrosion structures is essential, since exposing reactive layers, such as bronze disease, may accelerate deterioration. For this reason, laser cleaning should only form part of a broader conservation strategy grounded in scientific analysis and long-term preservation goals (Di Francia et al., 2022).

From a critical standpoint, laser ablation, like any other mechanical cleaning method, cannot be considered neutral or risk-free. Its irreversible nature and potential to affect stability or perception demand careful planning, preliminary testing, detailed documentation, and a deep understanding of the object's history.

In practice, laser cleaning is just one of several possible approaches. Cleaning is only the first step in a broader conservation process that must also address chemical stabilisation and final protective treatments (Robbiola, Fiaud, & Pennec, 1993). Within this framework, innovative alternatives such as retentive matrices are emerging, combining physical cleaning with controlled release of chemical agents to reduce overall aggressiveness and improve long-term stability.

8.4.4 Chemical cleaning in bronze conservation: solvents, retentive media and chelating agents

Chemical methods play a central role in the conservation of copper alloys, especially when surface alterations are too active or complex to be treated only with mechanical methods. Their advantage lies in the ability to act selectively on corrosion products through controlled reactions, allowing deeper and more effective interventions when applied according to rigorous technical standards.

Among the most persistent challenges is the presence of chlorides, which can trigger *bronze disease*. This progressive process, marked by the formation of copper hydroxychlorides and their self-catalytic spread, compromises both the stability and the appearance of the object, sometimes leading to irreversible material loss if left untreated.

Research has long sought effective methods for chloride removal. One classical reference is McLeod (1987), who compared seven treatments applied to archaeological objects recovered from marine contexts. He concluded that alkaline dithionite baths were the most effective, as they reduced copper (II) hydroxychlorides into less reactive compounds and sometimes even metallic copper. The characteristic chocolate-brown colour on treated surfaces indicated successful stabilisation.

However, these treatments require controlled laboratory conditions and advanced expertise, which restricts their application outside specialised institutions. Practical limitations also arise for medium- or large-scale objects, where immersion baths are difficult to control. Direct application of liquid agents on extensive surfaces may also cause unpredictable reactions due to limited regulation during treatment.

To address these constraints, especially in localised interventions or on complex geometries, new supports have been developed to deliver chemical agents in a controlled way. These include solvents, colloidal and gel-based systems, and chelating agents, which are discussed in the following subsections.

8.4.4.1 Cleaning with solvents

In bronze conservation, solvents are mainly used in two contexts: to assist the mechanical cleaning of corroded surfaces and to remove aged protective coatings. In both cases, their role is to enable controlled and selective interventions, avoiding unnecessary alteration of stable patinas and the metal substrate (Jedrzejewska, 1961).

The most common solvents include *white spirit, ligroin, ethanol, isopropanol, cyclohexane* and *acetone*. They are often applied in order of increasing volatility, and sometimes at higher temperature, as with white spirit or ligroin. Application methods vary, ranging from swab cleaning and cellulose poultices to gel-based systems (García-Cuetos et al., 2023; Matteini et al., 2003; Petiti et al., 2020; Salvadori et al., 2014; Zappa, 2017). These approaches allow gradual and selective cleaning, with good control over contact time and depth of penetration.

In mechanical cleaning, solvents are useful for removing greasy dirt, degraded waxes and hydrophobic residues. This increases the efficiency of the intervention and reduces the risk of abrasion to stable patinas (Petiti et al., 2020; Zappa, 2017).

For the removal of aged coatings, solvents dissolve waxes or synthetic polymers previously applied as protective films, acting only on the surface without directly affecting the bronze (Salvadori et al., 2014). In some cases, *white spirit* is used not as a cleaner but as a formulation solvent for applying microcrystalline wax.

8.4.4.2 Colloidal and Gel-Based Media: Controlled Delivery Systems for Cleaning Treatments

In the conservation of sensitive surfaces, retentive media for localised chemical application have gained increasing importance, particularly on porous or altered materials. These systems allow spatial and temporal control of solvents, chelating agents and cleaning solutions, minimising unwanted penetration and reducing the risk of altering original layers.

Among the most frequently used are colloidal systems such as *Laponite*™, a synthetic magnesium silicate clay that forms stable dispersions. Its high-water retention and buffering action (pH ≈ 9.3) enhance the effectiveness of chelating agents. These properties make it particularly suitable for the removal of corrosion stains caused by copper leaching onto stone substrates. It is valued for its easy removal and absence of visible residues (Canevali et al., 2024; D. W. Thompson & Butterworth, 1992).

Another approach is the use of film-forming polymers such as *polyvinyl alcohol* (PVA). Applied in aqueous or hydroalcoholic solution with plasticisers, PVA has been combined with EDTA as a retentive medium. When dry, it forms a flexible, peelable film that ensures prolonged surface contact while minimising penetration into porous substrates. After treatment, the film can be removed together with the spent reagent and corrosion products, providing precision and ease of use (Parisi et al., 2018).

Gel-based systems have become the most widespread alternative in the last decades, especially for heterogeneous surfaces or sensitive patinas. Initially developed for solvent application, they have evolved into more complex formulations capable of incorporating chelants and other active agents such as *ammonia*. This allows modulation of reactivity according to the treatment needs (Baglioni et al., 2009; Bescher & Mackenzie, 2018).

Active agents integrated into these gels include polar/non-polar solvents and surfactants, which facilitate the removal of greasy deposits by reducing surface tension and emulsifying residues. Their use in gels improves control of solvent action, reducing migration and wetting time, which is particularly useful on sensitive patinas (Petiti et al., 2020; S. M. Smith, 2017).

Among the most common gelling agents are *agar* and *gellan gum*, valued for their biocompatibility, transparency and ease of handling. They are applied hot and peeled off once solidified, ensuring good surface contact and minimal residue (Giraud et al., 2021). More recently, plant-based gels such as kudzu and konjac have been tested, showing effectiveness in removing copper ions from stone surfaces associated with sculptures. They have proved efficient, compatible and environmentally sustainable (Vázquez-de la Fuente et al., 2023).

The choice of retentive medium must consider surface sensitivity, coating stability, chemical compatibility and reversibility. These developments represent not only a technical improvement but also a conceptual shift towards more localised, controlled and material-respectful conservation.

8.4.4.3 Chelating Agents

Since the mid-20th century, chelating agents have been used in the conservation of metallic materials, valued for their ability to selectively remove corrosion products without damaging original surfaces (Burgess, 1991; Heuman, 1992). Their effectiveness lies in their capacity to form stable metal complexes and to show selectivity towards specific metal ions. This allows targeted removal of unwanted corrosion while preserving stable phases.

The term *chelating* derives from the Greek *chele* ("claw") and describes how the molecule surrounds and binds to a metal ion, isolating it from the environment (Carlyle et al., 1990). This makes chelators important tools for treating metallic surfaces and corrosion-related alterations, enabling controlled ion extraction.

Efficiency depends not only on the chemical structure of the chelator but also on pH, concentration, exposure time, application temperature and the delivery medium (Canevali et al., 2024). Careful adjustment of these factors maximises cleaning effectiveness and minimises the risk of over-cleaning. Chelator-based methods are particularly useful when corrosion is extensive or localised precision is essential (Basilissi et al., 2022).

In addition to the three most widely documented chelating agents (*EDTA, citric acid and Rochelle salt*), two other compounds are occasionally mentioned. *Diethylenetriaminepentaacetic acid* (DTPA) is used for the controlled removal of corrosion in buffered gels, which allow precise localisation and contact time (Loeper-Attia & Maniguet, 2017). However, its environmental persistence limits long-term suitability (Almubarak et al., 2022).

Oxalic acid, a crystalline, water-soluble dicarboxylic acid, has been used to clean copper alloys and natural stone (Alquera Ciencia SL, n.d.). It can dissolve corrosion deposits and, under certain conditions, precipitate copper as cupric oxalate. While effective, its aggressiveness risks damaging calcareous or sensitive materials, and it should only be used in controlled concentrations and under expert supervision (F. H. Edwards & Gailer, 1945).

EDTA

Ethylenediamine tetraacetic acid ($C_{10}H_{16}N_2O_8$), known as EDTA, is one of the most widely studied chelating agents in conservation due to its strong complexing ability and versatility (Bogojević et al., 2022; Ostertag, 1977; Parisi et al., 2017; Stelzner & Eggert, 2008).Its structure allows it to bind firmly to ions such as calcium, magnesium, iron and copper, producing stable, water-soluble complexes. This makes it particularly useful for removing reactive salts and corrosion products.

EDTA was synthesised in 1935 by Austrian chemist Ferdinand Münz as a substitute for citric acid in German industry. Although initially used in textiles, its strong chelating properties were quickly recognised. The 1942 patent, however, did not credit Münz due to restrictions under the Nazi regime (Paolieri, 2017).

Today EDTA is found in many everyday products: as a stabiliser in cosmetics, an antioxidant in food, and a softening agent in detergents and personal care products. This widespread use has raised concerns about its environmental persistence and ecological impact.

In conservation, EDTA has proved effective in removing unwanted patinas and metallic salt deposits, especially from copper alloys. It is particularly suitable for localised cleaning where preservation of the original surface is essential. Its use is well documented in both museum settings and outdoor interventions.

Environmental and health considerations: while dermal absorption is minimal (<0.001%) and it is considered safe in cosmetics (Federal Institute for Occupational Safety and Health-Notification Unit, 2004), EDTA has very low biodegradability. In 2023, the European Union limited its concentration in water to 60 µg/L (European Comission, 2023). Its persistence raises ecological concerns, especially in aquatic systems (Brusko et al., 2023).

EDTA has also been used in soil remediation, applied at 1% concentrations to extract heavy metals and assist in ecological recovery (Epunam & Emebese, 2023; Pastor Piñeiro et al., 2005).

Applications in conservation: studies confirm its efficiency in removing copper compounds from stone and bronze when applied in controlled systems. Giuliani et al. (2024) reported effective cleaning of calcareous stone using EDTA in PVA–borax gels with agarose, leaving no residues. Vázquez-de la Fuente et al. (2023) noted that konjac and kudzu gels with EDTA removed copper stains effectively, but caused significant calcium extraction, visibly altering the surface. Canevali et al. (2024) showed that a Laponite®, Arbocel® and 5% CMC matrix at pH 11.6 provided efficient cleaning without visible alteration. These findings demonstrate that EDTA's compatibility with calcareous materials depends strongly on the delivery system.

A summary of EDTA applications in conservation contexts is presented in Table 8.1.

Table 8.1 – Summary of application of EDTA as a chelating agent in treatments on bronze and stone.

Chelating Agent	Application method	Chelating agent concentration	pH	Results
EDTA	PVA-B + agarose	1.5 %	No specified. Assumed neutral to slightly alkaline (PVA-B system)	**Stone:** Very effective; no visible damage; best results on macroporous travertine
EDTA	Konjac/Kudzu	3 %	≈10	**Stone:** Highly effective, high Ca extraction
EDTA	Laponite® / Arbocel® / CMC	5 %	11.6	**Stone:** Effective, no visible damage

Source: Adapted from Giuliani et al. (2024), Vázquez-de la Fuente et al. (2023) and Canevali et al. (2024).

Citric Acid

Citric acid is a weak organic acid naturally present in many fruits and vegetables. With three acidic groups (pKa 3.1, 4.8 and 6.4), it progressively loses protons as pH increases. Under

neutral to slightly basic conditions, it exists mainly in negatively charged forms, which greatly enhance its affinity for metal cations such as copper. This explains its efficiency in forming stable copper complexes, a property that has been exploited in conservation treatments (Martínez et al., 2018).

In conservation–restoration, citric acid has been used since the mid-20th century, either alone or combined with other agents, particularly in the treatment of archaeological and ancient metals (Janes, 1965; Merk, 1978, 1981; Moncmanová, 2007; Organ, 1961). Its chelating strength is lower than that of EDTA, which makes it preferable when a milder agent is needed, for example in the removal of light or less adherent corrosion products.

This lower aggressiveness has also led to citric acid being evaluated as an alternative to EDTA in soil remediation, where it has shown effectiveness in extracting heavy metals while being more biodegradable (Di Palma & Mecozzi, 2007).

From a conservation perspective, the main advantage of citric acid is its selectivity and mild action, which reduces the risk of over-cleaning or damage to stable patinas. However, its lower strength also means longer application times and reduced effectiveness on strongly bound or thick corrosion layers.

Rochelle Salt

Sodium potassium tartrate ($KNaC_4H_4O_6 \cdot 4H_2O$), commonly known as Rochelle salt, is a double tartrate widely used in everyday products as a food emulsifier and pH regulator, and is also obtained as a by-product of winemaking (National Center for Biotechnology Information, n.d.).

In conservation, Rochelle salt has historically been employed for its moderate chelating capacity and gentle action on metal surfaces. It is particularly valued for selectively removing corrosion products such as cuprite without damaging delicate gilding. Its chelating

strength is weaker than that of EDTA or citric acid, which reduces the risk of over-aggressive cleaning but also limits its effectiveness on thicker corrosion layers (Matteini et al., 2003).

A well-documented case is the cleaning of the gilded elements of Lorenzo Ghiberti's *Porta del Paradiso* at the Opificio delle Pietre Dure. Concentrated Rochelle salt baths in neutral solution were used after preliminary treatments with acetone and distilled water, successfully preserving the gilded surface (Matteini et al., 2003).

Experimental trials by Matteini et al. (2003) tested different application methods. Standalone poultices with 35% solution were effective but slow, requiring long contact times and leaving some salt residues. Atomisation achieved high surface brightness but increased soluble salt accumulation. A combined method, Nd:YAG laser cleaning followed by a 10% poultice, proved more efficient, producing high reflectance with fewer residues and shorter treatment times. These results are summarised in Table 8.2.

In summary, Rochelle salt remains a historically reliable chelating agent for delicate surfaces. Its mildness makes it especially suitable for gilt bronzes, but its limited power against thick or complex corrosion layers restricts its use to carefully controlled contexts.

Table 8.2 – Summary of application of Rochelle salt as a chelating agent in conservation treatments on gilt bronze

Application method	Rochelle salt concentration	pH	Results
Poultice (standalone), degreasing with acetone. Applied for 6 h (3 renewals)	35 %	Neutral	Effective cleaning; slower; possible reddish spots; higher residual salts
Atomisation (standalone), degreasing with acetone. Applied during 3–4 h	35 %	Neutral	Highest specularity; high salt residues
Laser cleaning + poultice. Preliminary laser cleaning (300 mJ/cm²). Applied for 1 h	10%	Neutral	High reflectance; low residues; shorter treatment

Historical method – immersion bath (Opificio delle Pietre Dure)	Concentrated	Neutral	Selective cuprite removal; gilding preserved

Source: Adapted from Matteini et al. (2003).

8.4.4.4 Graffiti removal in bronze sculpture

Graffiti on bronze sculptures constitutes a recurrent form of vandalism, documented across diverse urban contexts and cultural settings. This unauthorised intervention causes both aesthetic and material damage, compromising the visual integrity of the artwork and sometimes accelerating deterioration processes.

Its impact is especially significant on outdoor sculptures, where the combined action of pollutants, humidity and solar radiation favours paint adhesion and ageing. Inadequate removal can lead to the irreversible loss of original layers, such as historical patinas or earlier protective treatments. For these reasons, the choice of cleaning methods must follow principles of minimal intervention, chemical compatibility, and strict control of the action exerted on the surface.

Among solvents, acetone is one of the most effective, particularly on surfaces with artificial patinas (Zycherman & Veloz, 1979). However, its effectiveness decreases on natural, powdery patinas due to deeper solvent penetration, which may cause irreversible changes. It can also partially remove synthetic coatings, making immediate reapplication of protection necessary. For precise control, the U.S. General Services Administration (2017c) recommends localised application with stencil brushes or cotton swabs, restricted to graffiti areas, followed by reapplication of the original coating. Chemical methods are often complemented by mechanical procedures to achieve complete removal, especially when paint layers are strongly adhered or aged.

Alternative physical methods include dry ice blasting, which reduces paint adhesion by thermal shock. While effective on bare metals, studies show it also removes part of the patina or corrosion layers, limiting its applicability (van der Molen et al., 2011; Vega-Bosch et al., 2024).

Preventive approaches have been explored, such as wax-based anti-graffiti coatings designed to reduce paint adhesion. Laboratory tests on coatings composed of 5–10 wt% acrylic polymer, 10–20 wt% polyolefin waxes and 70–80 wt% water demonstrated not only effectiveness against graffiti, but also conservation benefits: no adverse effects on patina, protection from dissolution, and improved corrosion resistance (Goidanich et al., 2010). However, once degraded, protection declines, and in thin layers degradation occurs faster, requiring annual reapplications. They also tend to attract dirt, shortening intervals between cleanings. Effectiveness is generally greater on unpatinated bronzes than on patinated ones.

Today, both preventive and curative options are available on the market. Preventive methods, offered by specialised companies, include paraffin polymer emulsions that protect against varnishes, spray paints and graffiti. Curative cleaning products include gels based on ether glycols and surfactants (CTS Europe, 2015), tested on stone and also recommended for metals. In all cases, controlled testing on discreet areas is essential to assess surface response, compatibility and actual effectiveness before full-scale intervention.

8.4.5 Inhibitors

Among the resources employed to mitigate the deterioration of heritage metal objects, corrosion inhibitors have acquired a prominent role, both for their stabilising capacity and their potential compatibility with already altered surfaces.

Corrosion inhibitors are chemical substances which, when applied to the metal surface at an appropriate concentration, can significantly reduce the rate of the corrosion process (Ferrari,

2021; Rocca & Mirambet, 2007; Stupnisek-Lisac et al., 2007; 2017). Their action is based on the modification of the physicochemical state of the metal surface (Cano & Lafuente, 2013; Trabanelli & Carassiti, 1970), resulting in the formation of a protective layer or film that limits contact with the corrosive environment (Abdelbar, 2024; Rotaru et al., 2010; Zappa, 2017).

According to Monticelli (2018), these films can be classified into three main types: passivating, precipitation, and adsorption films, whether physical or chemical.

Passivating films are compact and adherent, usually 30–200 Å thick. They are generated by oxidising inhibitors such as chromates and nitriles, though these are no longer used in conservation due to their toxicity.

Precipitation films result from reactions between the inhibitor and soluble species present in the environment, or with ions released by the metal. Benzotriazole (BTA) is the most representative example. Although these films may be porous or not perfectly adherent, they still provide effective protection.

Adsorption films are subdivided into physical and chemical adsorption. In physical adsorption, inhibitors, mainly organic compounds, adhere to the metal surface through electrostatic forces, producing a reversible layer mediated by a thin film of water molecules between the inhibitor and the substrate. However, their efficacy tends to decrease as temperature increases. Examples include quaternary ammonium salts and nitrogen-based compounds such as triazoles. In chemical adsorption, strong bonds are formed between the inhibitor and the metal through electron exchange or sharing. This process can promote polymerisation on the surface, reinforcing the protective film. Unlike physical adsorption, chemical adsorption is not reversible; inhibitors based on oxines and phosphonates belong to this category

Unlike industrial contexts, where inhibitors are applied to clean surfaces as a preventive measure, in conservation they are usually applied to surfaces that already present a patina or corrosion layer, which must be respected due to their historical and aesthetic value (Cano &

Lafuente, 2013; Ferrari, 2021; Rocca & Mirambet, 2007). This difference directly affects both the choice of inhibitor and its effectiveness.

Effectiveness depends on factors such as the characteristics of the metal, the inhibitor's chemical structure, environmental conditions, and the type of corrosion products present (Brunoro et al., 2003; Fateh et al., 2020; Kosec et al., 2010; Zappa, 2017). Inappropriate selection may reduce effectiveness or alter patinas. For this reason, preliminary cleaning and degreasing are often recommended to ensure adhesion and film stability.

Concentration is also critical. Some inhibitors achieve high protection even at low concentrations, while others require careful adjustment to avoid negative side effects (Biswal et al., 2024; Gravgaard & van Lanschot, 2012; X. Wang et al., 2014).

Overall, corrosion inhibitors remain a key but delicate option in the stabilisation of metallic heritage. Their use requires rigorous evaluation of each object's specific conditions and potential interactions with pre-existing materials. These considerations make inhibitors one of the most technically and ethically debated areas in current bronze conservation.

8.4.5.1 Benzotriazole (BTA)

Among corrosion inhibitors developed for various applications, benzotriazole (BTA) is the most extensively studied and commonly used in the conservation of copper-based heritage objects. Its widespread adoption is due to a combination of proven efficacy, moderate cost, relative ease of application, and strong documentation in both scientific and conservation literature.

Benzotriazole ($C_6H_5N_3$) is an organic compound that has been used since the 1950s in a wide range of industrial, medical, agricultural, commercial, and domestic applications. Its structure consists of a fusion between a triazole ring ($C_2H_3N_3$) and a benzene ring (C_6H_6) (Cantwell et al., 2015).

Its anticorrosive properties lie in its ability to react with copper surfaces to form insoluble Cu-BTA complexes that generate a passive protective layer (Mamaş et al., 2005). Since its formulation, BTA has been investigated for its effectiveness in protecting copper and its alloys (Cotton & Scholes, 1967; Dugdale & Cotton, 1963). In industrial contexts, it is widely applied in both dry and aqueous environments, such as heating and cooling systems, where it acts as a reliable passivating agent for copper piping (Khadom et al., 2010; Lee et al., 2021; Wiklund, 2007).

Various BTA-based formulations have been developed to adapt to aggressive environments, including acid rain and prolonged immersion, with performance varying according to alloy composition and environmental conditions (Fan & Katritzky, 1996; Khan et al., 2015; Simonović et al., 2020). In cultural heritage conservation, BTA has gained relevance due to its ease of application and relatively predictable performance under controlled conditions (Dermaj et al., 2007).

Despite the concerns outlined below, BTA remains the most widely employed corrosion inhibitor in conservation-restoration, owing to its superior efficacy when compared to other available compounds. It is typically applied as a 3% solution in polar solvents such as ethanol or acetone or incorporated into other products to enhance their inhibitory performance. One example is Incralac™, a formulation combining BTA with acrylic resins, discussed in section 8.4.6.

Its introduction into conservation began in the mid-20th century. Organ (1963) applied it to Roman coins, but issues such as darkening and weight increase led to its initial dismissal, although he recognised its potential under specific conditions. Madsen (1971) demonstrated its effectiveness on clean copper and lightly corroded bronze, but in advanced cases with chloride hydroxides, BTA performs poorly unless applied under vacuum or heat, techniques rarely feasible for large outdoor sculptures.

BTA's widespread adoption accelerated in the 1980s, with numerous patents reflecting its expanding role (Fan & Katritzky, 1996). This growth was driven not only by technical

performance but also by increasing demand for chemical solutions that could be integrated into systematic conservation protocols.

Effectiveness and Limitations of BTA in Copper Alloy Sculpture

BTA's ability to form stable Cu-BTA complexes provides effective corrosion resistance (Cantwell et al., 2015; Cao et al., 2002). Combinations with quaternary salts or surfactants improve its action under adverse conditions like high humidity or rainfall (Gelman et al., 2014; Simonović et al., 2020; Wan et al., 2023; Žerjav & Milošev, 2015). It also protects surfaces with carbonaceous residues, acting at the interface with the clean metal (Lee et al., 2021).

Still, limitations persist. Surface darkening is frequently reported (Albini et al., 2018; Faltermeier, 1997). Achieving a homogeneous film requires prolonged exposure, rarely practical for large-scale sculpture (Albini et al., 2018). Effectiveness also declines on alloys containing metals other than copper. Ni-BTA films on nickel lack compactness, while film formation on zinc is slow, reducing protection on copper–zinc alloys such as brass. In tin bronzes, higher tin content interferes with uniform protective film formation (Abdullah et al., 2006; Abu-Baker et al., 2013; P. G. Cao et al., 2002; Fenelon & Breslin, 2001).

The long-term reliability of BTA is also debated. In polluted urban environments, Cu-BTA layers can gradually lose cohesion, reducing durability (Albini et al., 2018). Moreover, its application on monumental bronzes is impractical due to the need for prolonged immersion (Brunoro et al., 2003; Laguzzi & Luvidi, 2010). Research into BTA derivatives aims to address these weaknesses, developing more stable, hydrophobic films with improved protective function.

Toxicity and Environmental Considerations of BTA

BTA must be handled with care. The ILO recommends local air extraction, gloves, and protective eyewear. It decomposes at 260 °C, releasing toxic vapours such as aniline and nitrobenzene (Organización Internacional del Trabajo & Organización Mundial de la Salud, 2018).

Although it has been used for over seventy years, its environmental impact raises serious concerns. BTA is regarded as a potential persistent organic pollutant (POP), resistant to degradation in soil and sediment, with bio accumulative potential and aquatic toxicity (European Chemical Agency ECHA, n.d.). It is also classified as a suspected endocrine disruptor (Federal Institute for Occupational Safety and Health, 2021), broadening its risk profile beyond technical performance to include human health and ecological sustainability.

From an ethical conservation perspective, these findings encourage a re-evaluation of BTA, especially where safer and more sustainable alternatives exist. Conservation today must look beyond immediate technical effectiveness to include the ecological and health footprint of the materials employed.

8.4.5.2 Other inhibitors

In light of increasing concerns regarding the toxicity of benzotriazole (BTA), research has focused on finding corrosion inhibitors with comparable performance but lower toxicological impact. Compounds such as 2-amino-5-mercapto-1,3,4-thiadiazole (AMT), 2-mercaptobenzothiazole (MBT) and 2-mercaptobenzimidazole (MBI) have shown high effectiveness in inhibiting bronze corrosion in acidic environments (Faltermeier, 1999; Ying et al., 2003; D.-Q. Zhang et al., 2003).

Among these, AMT is particularly notable for its performance in the presence of cuprous chloride (CuCl), the key agent responsible for bronze disease. It has a distinctive ability to remove this compound in powder form without damaging surface details such as inscriptions or decorative elements, thereby preserving the legibility and visual integrity of treated objects (Ganorkar et al., 1988; Ying et al., 2003).

In comparative studies with BTA, AMT demonstrated nearly equivalent inhibitory effectiveness, achieving a significant reduction in corrosion rates on immersed samples (Ying et al., 2003). More recent work has tested AMT in combination with other agents. For example, an aqueous solution of AMT and EDTA has shown improved corrosion resistance on artificially corroded bronzes, producing a more uniform protective layer, higher contact angle, and better performance than AMT alone (Jiang et al., 2025).

Cysteine ($C_3H_7NO_2S$), a naturally occurring amino acid, has also been studied as a cathodic corrosion inhibitor for archaeological copper alloys. It has shown effectiveness even under adverse conditions such as the presence of chlorides and high humidity, both typical of bronze disease (Gravgaard & van Lanschot, 2012; Messina et al., 2021).

Its molecular structure contains amino ($–NH_2$), carboxyl (–COOH), and thiol (–SH) functional groups, allowing it to carry both positive and negative charges within a pH range of 1.91 to 8.16. This versatility enhances its adsorption onto metal surfaces under acidic conditions. Despite its structural simplicity, cysteine exhibits high inhibitory performance, even at low concentrations (Gravgaard & van Lanschot, 2012; Messina et al., 2021).

Cysteine has been evaluated as a non-toxic alternative to BTA, particularly under high humidity conditions, where it has demonstrated comparable inhibitory efficiency. Its resistance to chlorides and reduced environmental impact are notable advantages. However, it has a higher risk of causing surface darkening, so its use is best limited to contexts with minimal exposure of bare bronze surfaces (Gravgaard & van Lanschot, 2012).

Its effectiveness has also been shown to increase when combined with other materials, particularly chitosan. One protocol involves applying cysteine first and then coating the

object with a chitosan-based layer, which prolongs the inhibitor's action, stabilises the coating, and preserves the aesthetic qualities of the metal (Messina et al., 2021).

The results of these AMT and cysteine tests are summarised in Table 8.3.

Table 8.3 - Comparative evaluation of corrosion inhibitors for copper-based heritage materials under controlled experimental conditions.

Inhibition Agent	concentration	Conditions	Results
AMT	7.5 mMol/L (1 g) in an aqueous solution with 5% citric acid (pH ≈ 2)	immersion for 12h at 25ºC	97% reduction in corrosion
AMT + EDTA	Solution of 5 mMol/L of AMT (0.666 g) and 10 mMol/L of EDTA (3.7 g)	Immersion for 12h at 25ºC	Improved corrosion resistance, formation of a uniform protective layer, and increased contact angle.
Cysteine	0.15 M in water	Exposure to 75% RH for 126 days; electrochemical tests with NaCl addition	50% inhibition; good stability in presence of chlorides; noticeable colour changes if exposure time is exceeded
Cysteine (after pre-treatment) + chitosan	2 mM (0.25 mg/mL)	Copper alloy pre-treated with 0.02 mg/mL cysteine for 30 min., then coated with 2 mM chitosan/cysteine. Exposed to HCl vapours for 180 and 250 min.	No corrosion after 250 minutes. Stable coating with no bubbles. Best protection and aesthetics.

Sources: Data adapted from Gravgaard & van Lanschot, 2012; Messina et al., 2021; Jiang et al., 2025 and Ying et al., 2023.

Other inhibitors, such as chromates and nitrites, have been progressively abandoned due to their high toxicity (Biswal et al., 2024; Ferrari, 2021). In general, commercially available inhibitors still include compounds with significant toxicological profiles, posing risks to both

the environment and conservation professionals (D.Q. Zhang et al., 2003). Current research is therefore focused on developing alternatives that provide effective corrosion protection with lower environmental and health risks. This shift reflects the broader evolution of conservation science towards safer, more sustainable practices, including so-called green techniques, which are discussed in detail in section 8.5.

8.4.6 Coatings

Protective coatings play a crucial role in the conservation of bronzes, particularly in sculptures exposed to outdoor environments where degradation is accelerated. As discussed in Chapter 6, outdoor bronze sculptures are especially vulnerable to factors of corrosion, which can lead to significant material loss and visible alteration of appearance (Artesani et al., 2020; Letardi, 2021; Pellis, 2025). While some natural patinas may provide partial protection, atmospheric pollution, solar radiation, humidity and climatic fluctuations, particularly in industrial or coastal areas, create conditions where specific protective treatments are essential (Mikić & Otmačić Ćurković, 2023).

Coatings act as physical barriers, reducing the permeability of the metal surface to aggressive agents. Their effectiveness depends on factors such as film thickness, adhesion, and, in some cases, the incorporation of corrosion inhibitors that provide active and long-lasting protection (de Luna et al., 2016; Rosetti, 2015). However, choosing and applying coatings remains a complex task, as conservators must balance protective efficiency with respect for the artwork's original aesthetic and ensure, whenever possible, the reversibility of the treatment (Artesani et al., 2020; de Luna et al., 2016; Mihelčič et al., 2019).

Over time, formulations have evolved from traditional waxes and synthetic resins to innovative materials incorporating nanotechnology. Current research focuses on coatings that are durable, less toxic, easier to apply and, above all, reversible (Brostoff, 2003; Mihelčič et al., 2019; Mikić & Otmačić Ćurković, 2023). This development aligns with

sustainability principles, favouring products derived from natural raw materials, with low toxicity and full compatibility with the artwork, the environment and human health.

Molina et al. (2023) identify six main groups of coatings used in bronze protection: waxes, acrylic resins, nitrocellulose lacquers, carboxylates, fluoropolymers and organosilane systems. Waxes include microcrystalline and polyethylene waxes; acrylic resins include commercial products such as Incralac™ and Paraloid™; nitrocellulose lacquers include Agateen™; carboxylates feature compounds such as sodium decanoate; fluoropolymers cover various commercial formulations; and organosilanes include both individual products and organic–inorganic hybrids.

Despite the diversity of laboratory-tested formulations, results from the questionnaire presented in Chapter 7 indicate a clear preference in conservation practice for traditional options. Acrylic resins and waxes remain the most widely used products for bronze protection, while fluoropolymers, organosilane systems, carboxylates and other innovative formulations are still mainly explored in research contexts.

8.4.6.1 Incralac

Incralac is a clear acrylic lacquer designed to improve corrosion resistance and retain the bright, unaltered appearance of copper and its alloys. It offers strong initial protection and acts as an effective barrier against atmospheric corrosion and tarnish in outdoor environments. A pioneering product in the coatings field, it has remained widely used since its development and continues to be a reference for the protection of outdoor bronze sculpture (Marsden, 1972; Wolfe et al., 2017).

Incralac was developed in 1964 as part of a research programme led by the International Copper Research Association (INCRA), now the International Copper Association (ICA), in collaboration with the British Non-Ferrous Metals Research Association (BNFMRA) (Boyatzis et al., 2017; Masi et al., 2019). Its main goal was to provide longer-lasting

protection than the existing products of the time, which rarely exceeded six to twelve months of outdoor performance (Wolfe et al., 2017).

The formulation includes Paraloid™ B-44, benzotriazole (BTA) and Paraplex G-60. Paraloid™ B-44 is a copolymer of methyl methacrylate with minor ethyl and butyl acrylate units. BTA functions as a corrosion inhibitor and UV absorber, while Paraplex G-60, an epoxidised soybean oil plasticiser, improves film flexibility (Bierwagen et al., 2003; Hallstar Industrial, n.d.; Marsden, 1972; Wolfe & Grayburn, 2017).

Incralac can be applied by immersion, brushing or spraying. Spraying is generally preferred, since brushing often leaves thin areas that encourage corrosion and produce streaks. The optimal dry film thickness is 25–30 μm; above this level, the surface can appear excessively glossy or "lacquered". Polyethylene dispersions may be added to moderate gloss (Marsden, 1972; U.S. General Services Administration, 2016; Wolfe & Grayburn, 2017).

Early expectations suggested an outdoor service life of around two years. In practice, performance often reaches three to five years, and up to nine when combined with wax topcoats and maintained (Brostoff, 2003; Craine et al., 1992; McNamara et al., 2004). Wax application also helps to moderate gloss.

Over time, Incralac loses effectiveness, in large part due to peroxide formation beneath the film and UV-induced degradation of retained solvents and volatile compounds from Paraloid™ B-44. The degradation of these solvents also makes Incralac susceptible to biodeterioration (Down et al., 1996; McNamara et al., 2004; Barucha & Baker, 1965, apud Wolfe & Grayburn, 2017). Another reported cause of ageing is the gradual loss of BTA, possibly by sublimation, during outdoor exposure (Boyatzis et al., 2017; Brostoff, 2003; Scott, 2002).

Removal becomes inconsistent as the coating ages. Reports indicate that it can become partially insoluble, likely due to crosslinking and the loss of BTA. Alternative methods such as laser cleaning or CO_2 blasting have been explored, though they remain inaccessible for

many practitioners due to their high cost (Brostoff, 2003; Dajnowski & Lins, 2010; Reiley, 2017; Salvadori et al., 2014; Sansonetti et al., 2015).

The effectiveness of Incralac varies according to factors such as object structure, patina type, exposure conditions and manufacturer's formulation. As a result, studies report contradictory outcomes both in laboratory tests and field applications (Boyatzis et al., 2017; Molina et al., 2023; Wolfe & Grayburn, 2017). Another limitation is its moderate resistance to abrasion and mechanical stress (Dumont & Thiery, 2001).

Finally, the presence of BTA raises health and environmental concerns (European Chemical Agency ECHA, n.d.; Masi et al., 2019; Shi et al., 2019). Despite these criticisms, Incralac remains widely used, supported by conservators' familiarity with the product and its historically central role in conservation practice (Wolfe & Grayburn, 2017).

8.4.6.2 Alternatives to Incralac

The search for substitutes for Incralac responds to several concerns: its variable durability in outdoor environments, the difficulty of removal after ageing, issues with gloss control and, most notably, the presence of BTA. The aim is to develop coatings that are more stable and less toxic, with good adhesion, controlled aesthetics and, whenever possible, reversibility through safe methods.

Acrylic coatings. Alternatives based on acrylic polyurethanes have been studied, such as Nikolas 9778 Exterior Uralac and BASF 923-85, regarded as high-performance due to their outdoor durability (Brostoff, 2003; De la Rie et al., 1999). Along the same line, Nikolas 11565 Exterior, a modified acrylic based on B-48, incorporates BTA and UV absorbers, reducing surface irregularities associated with application, particularly in thin films (Brostoff, 2003).

Among the low-VOC options, a water-based variant of Incralac has been developed. Although its protective effectiveness is lower than that of the solvent-based formulation, it

is recommended for bronzes with unpatinated surfaces and not advisable for patinated ones. Unlike the original Incralac, this product can be dissolved with the stripper n-methyl pyrrolidine ($C_5H_{11}N$), a highly toxic solvent whose risks limit its real applicability in heritage contexts (National Center for Biotechnology Information, 2025; Talas, n.d.).

Other acrylics such as Pantarol™, produced by Edelweiss Industrielacke Lutzenberger GmbH, allow dissolution and cleaning with products from the same line. Studies on metals have shown very favourable anticorrosive performance on unpatinated surfaces, even surpassing Incralac in thin films (Heginbotham et al., 2014). However, their relatively high cost and limited availability outside central Europe restrict their use among small institutions or independent conservators.

Among the most noteworthy products that can replace Incralac is Permalac™, based on the resin Paraloid™ B-48N, which substitutes the traditional B-44. This change provides greater hardness, improved abrasion resistance and optimised adhesion to the metal. Its satin version has shown good performance in terms of corrosion resistance, impedance and appearance (Wolfe et al., 2017). B-48N itself is also regarded as a valid alternative owing to its higher molecular weight and adhesive effectiveness on both patinated and unpatinated bronzes (Brostoff, 2003; Molina et al., 2023; Wolfe et al., 2017).

Fluoropolymers have also been explored as protective coatings. Systems based on FEVE (fluoroethylene/vinyl ether) have been investigated in both solvent- and water-based formulations, with particular attention given to their removability, a key requirement in conservation. The incorporation of POSS nanoparticles improves the hydrophobicity of the films and their resistance to moisture, without significantly altering surface appearance (Clare & Swartz, 2015; Mihelčič et al., 2019).

Another fluoropolymer of interest is Kynar™ (PVDF), which, when combined with traditional acrylics such as Paraloid™ B-44 or A-21, demonstrates improved adhesion and initial corrosion resistance (Bierwagen et al., 2003; Clare & Swartz, 2015). Nevertheless, its insolubility in common solvents makes removal extremely difficult, compromising reversibility, which remains a core principle in conservation practice (Artesani et al., 2020).

Silane compounds and organosilane hybrids. Within this field, PropS-SH, an inhibitor of pyrite formation, has shown greater efficiency than Incralac under acid rain conditions (Balbo et al., 2012; Chiavari et al., 2013; Feng et al., 2023; Yang et al., 2021).This compound forms continuous and homogeneous layers, with good penetration into patinated surfaces when applied by spraying. It also offers UV resistance with minimal chromatic variation and establishes thiolate bonds with copper, thereby improving adhesion (Artesani et al., 2020; Masi et al., 2019; Molina et al., 2023).

In the same line, hybrid coatings such as ORMOCERs and OrmoSils containing SiO_2 have been developed. These materials combine an inorganic silica matrix with organic functional components, showing good adhesion and barrier effect. Films incorporating SiC and CeO_2 nanoparticles have demonstrated improved compactness and adherence (Bescher & Mackenzie, 2003). However, ORMOCERs are not fully reversible, sometimes requiring mechanical removal (Pilz & Römich, 1997).

Biopolymers. In keeping with current trends towards sustainable formulations, coatings based on biopolymers such as chitosan or HAVOH/GP have been developed, incorporating inhibitors such as BTA or MBT. In some cases, these inhibitors are encapsulated to achieve sustained release. Results show barrier improvements superior to the use of BTA alone (Artesani et al., 2020; de Luna et al., 2016).

Although research provides a wide range of alternatives to Incralac with potential advantages in terms of stability, toxicity and sustainability, their adoption in professional practice remains limited. High cost, technical barriers, and insufficient documentation of long-term performance explain why many institutions continue to rely on traditional coatings such as acrylics and waxes. This gap between experimental development and actual implementation in conservation practice highlights the need for further collaborative research and field validation.

8.4.6.3 Waxes

The use of waxes as protective coatings on metals is considered one of the earliest standardised practices in conservation. Their application responds to the dual need of providing a physical barrier against environmental agents and enhancing the visual appearance of metallic surfaces.

In the specific case of bronze objects, waxes have been widely employed due to their ability to form an effective film that limits the penetration of moisture and oxygen into the metallic substrate (L. S. Selwyn et al., 1996). This protective layer also prevents the intrusion of airborne pollutants and helps to reduce the risk of surface alterations caused by handling or vandalism. In this way, waxes function both as a direct protective medium and as a sacrificial layer that delays the deterioration of underlying protective systems such as acrylic resins (N. Baer, 1988; Moffett, 1996).

Beyond their strictly protective function, waxes have also been applied for aesthetic purposes. Their use helps to homogenise the appearance of metallic surfaces, reducing unwanted gloss and producing a more uniform tone. In some cases, pigmented waxes are deliberately applied to adjust or harmonise the colour of bronze objects, improving their legibility and integration in museum or urban contexts.

Microcrystalline waxes

Microcrystalline waxes are by far the most widely recommended and employed protective coatings in the conservation of metallic cultural heritage objects (Biribicchi, Macchia, et al., 2023; Brostoff, 2003; Jáuregui-Gonzalez et al., 2016). Derived from petroleum refining, they are composed mainly of saturated long-chain hydrocarbons, usually between twenty and fifty carbon atoms, in linear, branched, and cyclic configurations. This structural diversity produces very small crystals and an almost amorphous appearance, resulting in

greater flexibility and reduced brittleness compared with paraffin waxes (Brostoff, 2003; Swartz & Clare, 2015). Within the film, more ordered crystalline regions provide stability, while amorphous regions contribute cohesion and elasticity. The hydrophobic character of these compounds explains the low permeability of the wax to water and corrosive ions, a fundamental property for its effectiveness as a protective barrier (Brostoff, 2003; Swartz & Clare, 2015).

Microcrystalline waxes typically melt between 80 and 100 °C, which contributes to their stability under normal environmental conditions but limits their resistance under extremely high temperatures (Watkinson, 2010). Some commercial formulations incorporate polyethylene to increase hardness and raise the melting point, although this addition makes subsequent removal more difficult. Heating during application can modify the degree of crystallinity, altering the hardness and homogeneity of the film, which underlines the importance of the application technique in conservation practice (Brostoff, 2003; Considine et al., 2010; Jáuregui-Gonzalez et al., 2016).

Among the most commonly used products are Cosmoloid H80 and Renaissance Wax™, developed at the British Museum in 1968 and widely disseminated in the museum environment (England et al., 2016; Kremer Pigmente, 2014; Molina et al., 2023; Watkinson, 2010). Other examples include R21™, a 10% dispersion in turpentine (Biribicchi, Macchia, et al., 2023; Joseph et al., 2007); TeCe 3534F™, produced by Tromm GmbH (Joseph et al., 2007; Molina et al., 2023); and Butcher's Wax™, a mixture of microcrystalline and carnauba wax (Molina et al., 2023; Swartz & Clare, 2015; U.S. General Services Administration, 2017a). Polyethylene emulsions such as BASF Poligen™ have also shown interesting behaviour on ferrous metals, while silicone waxes and nanowaxes have produced promising results in tests on archaeological bronzes (Abdullatef et al., 2022, 2023; Molina et al., 2023).

The method of application strongly influences the behaviour of the coating. Wax is usually spread in thin layers with a soft-bristle brush or cotton cloth on slightly warmed metallic surfaces, then polished after drying to control thickness and gloss (England et al., 2016; McIntonsh Simmonds, 2021; U.S. General Services Administration, 2017a). In other cases,

it is applied hot, using a heat gun or a gentle flame, which facilitates penetration into pores and cracks but may generate a more heterogeneous film and requires additional precautions to avoid damaging the metal or patina (Jáuregui-Gonzalez et al., 2016; McIntonsh Simmonds, 2021; U.S. General Services Administration, 2017b).

The use of microcrystalline wax presents clear advantages. Its hydrophobicity and low water vapour permeability make it suitable as a preventive protective coating (England et al., 2016; Swartz & Clare, 2015). It is particularly effective on patinated surfaces, where it remains in the pores of the patina and contributes to their stability (Letardi, 2004). It is also frequently used as a top layer over acrylic coatings such as Incralac, creating double-layer systems that combine the polymer's barrier properties with the hydrophobicity of the wax (Brostoff, 2003; England et al., 2016; Joseph et al., 2007; Watkinson, 2010). Even triple-layer systems, composed of wax, polymer, and another wax layer, have been tested, focusing instead on extending protection and delaying polymer degradation (Salvadori et al., 2014).

However, these advantages coexist with important limitations. The durability of the films is relatively short, usually between two and five years, which makes scheduled maintenance necessary. Over time, microcrystalline waxes are prone to photodegradation and oxidation, leading to loss of gloss, dust accumulation, and exfoliation (Biribicchi, Macchia, et al., 2023; England et al., 2016; Swartz & Clare, 2015). Their corrosion resistance is lower than that of other polymeric coatings, such as acrylics or urethanes, and impedance values for their films often fall below those considered optimal for true barrier behaviour (England et al., 2016). Moreover, hot application can increase the heterogeneity of the film (Swartz & Clare, 2015).

To these drawbacks must be added the difficulty of removal, which often requires solvents such as aliphatic and aromatic hydrocarbons, posing risks to both health and the environment. Removal is especially problematic when wax has penetrated the patina, particularly in the case of polyethylene-modified wax (Biribicchi, Macchia, et al., 2023; Considine et al., 2010; Moffett, 1996).

Recent research has further highlighted concerns about their indiscriminate use. For example, Renaissance Wax has been shown to accelerate corrosion in humid or saline

environments by retaining water at the metal–coating interface, raising questions about its suitability in outdoor or maritime contexts (Thickett & Stanley, 2019).

Microcrystalline wax therefore remains a useful resource in the conservation of bronzes, but it does not provide a permanent solution. Its role is better understood as an immediately practical option that enhances the protection of metallic surfaces, particularly when reinforcing inner protective layers such as Incralac.

Natural waxes

Natural waxes have traditionally been used as protective coatings in the conservation of metallic cultural heritage (Clarke, 1939; Morgan & Lodder, 1936). Among the most common is carnauba wax, of plant origin, present in some commercial formulations and often mixed with synthetic waxes and solvents, where it has shown a notable protective effect (Basso et al., 2020; Chelaru et al., 2015; Scott, 2002; Swartz & Clare, 2015). Beeswax, obtained from insects, was also widely used (Biribicchi, Macchia, et al., 2023).

Despite their prolonged use until the emergence of more recent protective methods, natural waxes have significant limitations. The most relevant is the production of organic acids during ageing in contact with moisture, which may promote corrosion. This problem is especially pronounced in animal waxes, which are more susceptible to acidic hydrolysis (Brostoff, 2003; Pellis, 2025). These limitations explain why natural waxes are no longer recommended for the protection of metals in heritage contexts.

In summary, the conservation of bronze sculptures relies on a wide range of methods that must respond to the complexity of the material and to the varied conditions in which these works are displayed. Surface cleaning, whether carried out with mechanical, chemical or combined techniques, is usually the first stage of intervention, but it must always be guided by careful diagnosis and preliminary testing to avoid over-cleaning or the loss of stable layers. Corrosion inhibitors and protective coatings provide additional means of

stabilisation, although their success depends on correct selection, controlled application and regular maintenance.

It is clear that no method can be considered neutral or universally applicable. Each technique carries potential risks as well as benefits, and its effectiveness depends on the conservator's ability to balance technical performance with respect for the historical and aesthetic integrity of the work. The results of this research, together with the survey responses, highlight the importance of combining professional expertise with analytical support and with long-term maintenance strategies.

Overall, the current repertoire of treatments demonstrates significant progress towards more precise and adaptable approaches. At the same time, it underlines the continuing need for critical reflection, comparative testing and the integration of new materials and technologies developed both within conservation and in related disciplines. The challenge is to ensure that these resources are not used as routine solutions but as carefully chosen interventions, adapted to the history and the specific condition of each bronze sculpture.

8.5 SUSTAINABLE ALTERNATIVES IN CONSERVATION OF BRONZES

The conservation of bronzes, like other areas of cultural heritage, now faces the challenge of incorporating sustainability into professional practice. The objective is not only to secure access to artworks in the present but also to ensure their transmission to future generations. This requires the development of methods and materials that are technically effective while presenting low toxicity, reducing risks for the object, the conservator, and the environment (Casaletto & Basilissi, 2017; Cuvillier, 2024; Del Curto & Turrina, 2023; Passaretti et al., 2021).

Scientific approaches in this field must therefore address ecological, economic, and social factors. This involves re-evaluating established practices, questioning the reliance on hazardous products, and pursuing research into safer alternatives (Casaletto & Basilissi, 2017). The challenge lies not only in improving the materials themselves but also in ensuring their practical feasibility across diverse institutional contexts and their acceptance within the profession.

Traditional methods for the conservation of bronzes, particularly chemical cleaning and inhibition, often rely on toxic reagents, generate polluting residues, and risk damaging fragile surfaces (Biribicchi, Giuliani, et al., 2023; Cuvillier, 2024). These limitations explain the increasing demand for alternatives that prioritise occupational health and environmental protection (Boccaccini, 2024; Cuvillier, 2024).

In response, recent research has promoted approaches inspired by green chemistry. These aim to minimise the use of aggressive solvents, favour biodegradable components, and ensure compatibility with original materials (Bandelli et al., 2024). Although still under evaluation in terms of effectiveness and large-scale applicability, such initiatives already demonstrate a shift in professional awareness. The perceptions collected in the questionnaire carried out in this research confirm the growing interest in sustainability, while also highlighting the gap between theoretical discourse and its consistent adoption in everyday practice.

Against this background, it becomes essential to analyse and validate new chemical approaches that combine technical efficiency with compatibility and environmental responsibility. In bronze conservation, such efforts have focused above all on cleaning processes, the development of sustainable solvents and chelating agents, and the search for alternative inhibitors and protective systems. These constitute the core themes of the following sections.

8.5.1 Sustainable Cleaning Methods in the Conservation of Bronze Objects

Cleaning remains one of the most delicate stages of conservation, as it directly affects both the stability of metallic surfaces and the visual perception of artworks. In Section 8.4.4, different gels and retentive media were introduced as effective supports for controlled cleaning. This section revisits some of those materials, such as konjac and kudzu, but with a distinct focus: their potential as sustainable alternatives. The emphasis here lies not only on their cleaning performance but also on their environmental profile, renewable origin, and biodegradability, which together make them promising candidates for greener conservation practice.

Polysaccharide-based hydrogels are among the most widely explored materials in this field. *Agar*, extracted from red algae such as *Gelidium*, *Pterocladia* and *Gracilaria* spp., has long been a reference material due to its accessibility and clean peel when properly applied. However, its relative rigidity, variable adhesion on irregular or vertical surfaces, and the risk of leaving residues have been reported, alongside sustainability concerns linked to large-scale algae harvesting and biodiversity impact (Cuvillier, 2024; Passaretti et al., 2021; São João et al., 2017; Vázquez-de la Fuente et al., 2023).

Konjac, derived from the tuber of *Amorphophallus konjac*, is one of the most promising substitutes. It rapidly forms a viscous gel at room temperature, facilitating preparation without the need for heating. Its adhesion on irregular surfaces, such as marble pedestals affected by copper run-off, has been highlighted in recent trials. Nonetheless, careful monitoring is required to avoid over-adhesion if the gel dries (Vázquez-de la Fuente et al., 2023).

Kudzu, extracted from *Pueraria montana* roots, offers a different set of advantages. It produces strong adhesion and versatility on complex or vertical surfaces, where agar often proves inadequate. It may also provide useful biocidal action during cleaning, though preparation typically requires heating and constant stirring to achieve homogeneous consistency (Cuvillier, 2024; Vázquez-de la Fuente et al., 2023).

Beyond plant-based polysaccharides, *bacterial biopolymers* have also been studied. Bacterial nanocellulose is renewable, biodegradable and has shown precise copper-stain cleaning on marble with minimal chromatic change (Sonaglia et al., 2024). *Gellan gum* provides transparency for visual control, and *xanthan gum* offers flexible handling; both, however, can leave residues that must be carefully removed (Canevali et al., 2024; Cuvillier, 2024).

Chitosan, obtained from chitin, is valued for good contact with rough surfaces and for metal-ion uptake, but thicker surface layers can hinder diffusion, limiting suitability in some treatments (Cuvillier, 2024).

In parallel, *organogels* have been developed for the immobilisation of organic solvents. Their main contribution lies in reducing volatility and broadening the range of cleaning agents that can be safely applied. Systems formulated with biodiesel and *dimethyl carbonate* (DMC), or based on *polyhydroxybutyrate* (PHB), illustrate how renewable and biodegradable matrices can deliver controlled solvent action (Bandelli et al., 2024; Passaretti et al., 2021; Yiming et al., 2019).

Within this group, low molecular weight gelators (LMWGs) offer a versatile and low-impact approach, as they immobilise solvents and reduce their release into the environment. Their sustainability, however, depends on the nature of both the gelator and the solvent employed, since not all are renewable or biodegradable. Silicone thickeners, for example, provide targeted solutions for water-sensitive contexts or for the removal of wax coatings, but require precise formulation and careful evaluation of long-term effects (Biribicchi et al., 2024).

Table 8.4 - Sustainable gels and organogels for cleaning applications in bronze conservation

Gel / Organogel	Properties	Advantages	Limitations	Environmental impact
Agar/Agarose	Polysaccharide from red algae; rigid	Widely used; reference in conservation	Low adhesion; brittle; possible residues	Dependent on algae; biodiversity risk
Kudzu	Plant-based polysaccharide	Strong adhesion; versatile on complex surfaces	Requires heating and mixing	Renewable
Konjac	Forms viscous gel at room temperature	Easy preparation; strong adhesion	Can adhere excessively if dried	Renewable
Bacterial nanocellulose (BC)	Biodegradable; high crystallinity	Precise cleaning; minimal chromatic alteration	Requires biotechnological production	Renewable; biodegradable
Chitosan	Natural polymer; polyelectrolyte	Flexible; good contact; metal uptake	Applied solid; may hinder ion diffusion	Renewable; biodegradable
Gellan gum	Transparent bacterial polysaccharide	Visual control; effective at low concentration	Fragile; possible residues	Renewable, low impact
Xanthan gum	Flexible bacterial polysaccharide	Smooth application; stable under varied pH/T. Good water retention	Leaves residues	Renewable, low impact
Organogel PHB-DMC/BD	Biopolymer with biodiesel & DMC	Effective for wax removal; solvent retention	Requires specific formulation	Based on biopolymers and green solvents
Oligopolyester + castor oil	Adjustable hydrophilic/hydrophobic balance	Removes resins and waxes	Still experimental	Renewable resource
LMWGs	Small molecules; self-assembly	Versatile; reduce solvent release	Limited mechanical stability	Low impact (depends on formulation)

Sources: Data adapted from Bandelli et al., 2024; Biribicchi et al., 2024; Canevali et al., 2024; Cuvillier, 2024; Passaretti et al., 2021; São João et al. 2017; Sonaglia et al., 2024; Vázquez-de la Fuente et al., 2023 and Yiming et al., 2019.

8.5.2 Sustainable solvents applied in the cleaning of bronzes

In recent years, attention has shifted towards sustainable solvents, developed from renewable resources and with lower risks for conservators and the environment. These alternatives have proved effective in removing waxes, varnishes, and surface deposits, offering safer methods while maintaining compatibility with sensitive metallic surfaces. Their adoption in conservation practice is still limited, but current research highlights their potential as substitutes for traditional, more hazardous solvents.

Dimethyl carbonate (DMC) is regarded as a green solvent due to its low toxicity, non-VOC classification, and biodegradability. It has been used in formulations for cleaning waxes from bronzes, often in combination with biodiesel to improve performance (Aricò & Tundo, 2010; Kuenen et al., 2016; Yiming et al., 2019).

Ethyl lactate (EL), derived from lactic acid, is used as a substitute for hazardous solvents such as toluene or xylene. It has shown effectiveness in removing terpenic varnishes and acrylic resins, such as Paraloid™ B-72, sometimes applied as a protective layer on bronzes, although its use on metals remains limited (Gu & Jérôme, 2013; Passaretti et al., 2024).

Other commercial products have also been explored. *Plurafac® LF 900*, a biodegradable, low-foaming non-ionic surfactant, is widely used in industry as a detergent and wetting agent for oils, greases, and organic soils. It has no affinity for copper ions and no direct anticorrosive effect, making it suitable only as a cleaning aid. *Trilon® M (MGDA)*, by contrast, is a biodegradable chelating agent employed in industrial metal-cleaning formulations for its ability to stabilise ions. While potentially useful for bronzes, its application requires caution: if not strictly controlled, MGDA may extract ions directly from the alloy (BASF, 2019; Haile, 2019; Kampasakali et al., 2021).

Fatty acid methyl esters (FAMEs), derived from vegetable oils, have been proposed as green solvents thanks to their biodegradability, low toxicity, and absence of VOCs. In conservation, they have shown good results in the removal of waxes and synthetic resins,

especially when applied in gel media that limit penetration and facilitate removal. Unlike their industrial use, where they may promote corrosion of copper alloys, in heritage contexts their controlled application avoids this drawback. They do not produce alkaline residues or require aqueous rinsing, which is an advantage over other solvents (Biribicchi et al., 2024; Rocha Jr. et al., 2019; Zaratti et al., 2024).

Other promising systems include *deep eutectic solvents* (DES), based on mixtures such as choline chloride with ascorbic acid. These are considered ecological and have been tested for bronze cleaning, usually with swabs or cellulose membranes. Results to date, however, have shown limitations, including incomplete removal of Cu(II) residues and loss of protective cuprite layers, which makes further refinement necessary before practical adoption (Tsurumaki et al., 2022).

Additionally, research has examined *biosurfactants* such as *rhamnolipids, sophorolipids, surfactin, saponins*, and *alkyl polyglycosides*. Already applied in industries like cosmetics, food, agriculture, and environmental remediation, these compounds are valued for their biodegradability and low toxicity. Some, such as rhamnolipids, have been studied as corrosion inhibitors, while *surfactin* and related biosurfactants have shown effectiveness in removing metal ions from soils and aqueous solutions (Farias et al., 2021; Mallik & Banerjee, 2022). Although their direct use in bronze conservation remains experimental, these findings point to a promising new direction for sustainable cleaning practices.

Table 8.5 summarises the main characteristics, advantages, and limitations of the sustainable solvents discussed, offering a comparative overview of their potential applications in bronze conservation.

Table 8.5 - Sustainable solvents applied to bronze cleaning.

Substance	Nature	Applications / Properties	Limitations / Notes
Dimethyl carbonate (DMC)	Organic carbonate, non-VOC	Removal of waxes; biodegradable; low toxicity	Often combined with biodiesel; requires gel formulation
Ethyl lactate (EL)	Lactate-based solvent	Substitute for toluene/xylene; effective on terpenic varnishes and acrylic resins (e.g. Paraloid™ B-72)	Limited validation on metals
Plurafac® LF 900	Biodegradable non-ionic surfactant	Removes oils, greases, and organic soils; surface cleaner	No anticorrosive action; auxiliary only
Trilon® M (MGDA)	Synthetic amino acid derivative, chelating agent	Ion stabiliser; industrial cleaner	May extract alloy ions; requires strict control
Fatty acid methyl esters (FAMEs)	Plant-derived esters	Removal of waxes and resins; biodegradable, VOC-free	Potentially corrosive in industrial use; safe in gels
Deep Eutectic Solvents (DES)	Mixtures (e.g. choline chloride + ascorbic acid)	Tested for bronze cleaning with swabs/membranes	Uneven cleaning; risk of cuprite loss; experimental
Rhamnolipids	Glycolipid surfactants from *Pseudomonas aeruginosa*.	Strong surface-active agents	Research still experimental; conditions must be controlled.
Sophorolipids	Glycolipid surfactants from yeasts (*Starmerella bombicola*)	Emulsifiers; widely used in cosmetics and detergents.	No direct studies on metals; activity depends on pH.
Surfactin	Natural glycosides from plants (*Quillaja saponaria*)	Foaming agents; long use in food and cosmetics.	No evidence on copper alloys; may leave residues.

Sources: Data adapted from Aricò & Tundo, 2010; Biribicchi et al., 2024; Farias et al., 2021; Gu & Jérôme, 2013; Kuenen et al., 2016; Mallik & Banerjee, 2022; Passaretti et al., 2024; Rocha Jr. et al., 2019; Yiming et al., 2019; Zaratti et al., 2024.

8.5.3 Sustainable chelating agents in the conservation of bronze

In the conservation of bronzes, it is essential to use cleaning agents that combine effectiveness with a low environmental impact. Conventional chelators such as EDTA, although highly effective, raise concerns regarding sustainability and the risk of damaging associated materials such as marble. This has encouraged the search for sustainable chelators, capable of acting selectively on copper corrosion products and iron deposits while at the same time reducing toxicity and persistence in the environment (Canevali et al., 2024; Cuvillier, 2024; Passaretti et al., 2021).

8.5.3.1 Reference chelators

Among natural organic acids, *citric acid* has been one of the most widely used in conservation for decades. Produced by fermentation of citrus fruits, it is valued for its biodegradability and low environmental impact, although it forms less stable complexes than EDTA (Angumeenal & Venkappayya, 2013; Canevali et al., 2024).

Gluconic acid, a weak acid that can be microbially produced (e.g. by *Aspergillus niger*), has shown better results than EDTA in cleaning copper alloys, especially when used in agar gels. Its strong affinity for calcium, however, limits its use on calcareous substrates such as marble (Ramachandran et al., 2006; Vázquez-de la Fuente et al., 2023).

Among more recent synthetic compounds, *ethylenediamine disuccinic acid* (EDDS) has been identified as a promising alternative. It shows strong copper ion sequestration and, unlike EDTA, is biodegradable within days, which makes it a rapid and more sustainable option for conservation contexts (Bucheli-Witschel & Egli, 2001; Zeremski-Škorić et al., 2010).

Other agents include biogenic compounds such as siderophores. *Deferoxamine* (DFO), produced by *Streptomyces pilosus*, has proved effective in removing iron deposits from bronze while interacting more gradually with copper, ensuring safer action on the substrate (Bellotti & Remelli, 2021; Cuvillier, 2024). Despite this, it remains less efficient than EDTA or EDDS and is costly to produce, as it is primarily intended for medical applications (Chiani et al., 2010; Keri et al., 2005).

Oxalic acid, another microbial metabolite (e.g. of *Beauveria bassiana*), reacts with corrosion products to form stable oxalates (moolooite). However, its complexes are less stable than those produced by synthetic chelators, and its acidity poses risks for sensitive substrates (Biswal et al., 2024; Canevali et al., 2024; Joseph et al., 2012).

8.5.3.2 Other sustainable alternatives

Beyond these reference agents, other molecules with metal-complexing ability have been explored.

Alanine, a natural amino acid, is biodegradable and of low toxicity. It forms stable complexes with divalent metals and has been proposed as a mild chelator for copper corrosion products on bronze, offering a more controlled action than stronger agents (Amino Acids Guide, 2024; Gaspar et al., 2013; Haynes, 2017; Macchia et al., 2023).

Glycine, the simplest amino acid, acts as a bidentate ligand and has been used in conservation since the 1990s. It is effective against atacamite but limited by its weak chelating strength and the need for thorough rinsing after use (Argyropoulos et al., 2021; Berthon, 1995; Gravgaard & van Lanschot, 2012).

Taken together, these sustainable chelators offer less aggressive alternatives to conventional agents, but their effectiveness varies according to the corrosion present and the sensitivity of

the substrate. Careful technical judgement is therefore essential in their selection and application.

Table 8.6 summarises the main properties, advantages, and limitations of the sustainable chelating agents discussed.

Table 8.6 - Sustainable chelating agents applied to bronze conservation

Substance	Nature	Properties / Applications	Limitations / Risks
Citric acid	Natural organic acid	Long used; removes copper corrosion and iron oxides on bronze; biodegradable	Forms less stable complexes than EDTA; may require longer application times
Gluconic acid	Natural organic acid (microbial origin)	Effective on copper corrosion; biodegradable; tested in gels	High affinity for Ca^{2+}; risks for marble and calcareous materials
EDDS (Ethylenediamine disuccinic acid)	Synthetic, biodegradable analogue of EDTA	More effective Cu^{2+} sequestration than EDTA; biodegradable within 3–4 days	Lower stability constants than EDTA; less documented in heritage contexts
Deferoxamine (DFO)	Microbial siderophore (Streptomyces pilosus)	Selective for Fe^{3+}; gradual action on Cu^{2+}; effective in removing iron deposits	Less efficient than EDTA/EDDS; costly; limited availability beyond medical field
Oxalic acid	Fungal metabolite (Beauveria bassiana, others)	Strong affinity with Cu(II); reacts with corrosion products to form oxalates	Complexes less stable than synthetic chelators; acidity risk
Alanine	Natural amino acid	Biodegradable; forms stable complexes with Cu^{2+}; mild chelator for bronze	Limited studies; effectiveness lower than stronger agents
Glycine	Natural amino acid	Simplest amino acid; effective on copper chlorides (e.g. atacamite); gentle action	Weak chelation strength; requires thorough rinsing

Sources: Data adapted from Angumeenal & Venkappayya, 2013; Biswal et al., 2024; Bucheli-Witschel & Egli, 2001; Canevali et al., 2024; Chiani et al., 2010; Cuvillier, 2024; Gaspar et al., 2013; Haynes, 2017;

Heuman, 1992; Joseph et al., 2012; Keri et al., 2005; Macchia et al., 2023; Ramachandran et al., 2006; Vázquez-de la Fuente et al., 2023; Zeremski-Škorić et al., 2010.

8.5.4 Sustainable inhibitors applied to the conservation of bronzes

The development of sustainable inhibitors and coatings has become one of the most promising lines of research in the conservation of historic metals. Unlike traditional inhibitors such as benzotriazole (BTA), which combine high effectiveness with significant toxicity, the current aim is to identify compounds that ensure protection while reducing risks for both the conservator and the environment (Abdel-Karim & El-Shamy, 2022; Argyropoulos et al., 2021; C. Giuliani et al., 2018; Privitera et al., 2023).These new materials are generally characterised by lower toxicity, renewable origin, and, in many cases, biodegradability, which makes them compatible with the principles of sustainable conservation (J. R. González-Parra & Di Turo, 2024; Sharma et al., 2023; Sivakumar & Srikanth, 2020; Zouarhi, 2023).

8.5.4.1 Plant extracts and vegetable oils

Among plant extracts, *Aloe vera* has shown remarkable performance, forming protective films on copper and bronze with inhibition values above 90% in saline and acidic media. Its polysaccharides, such as *acemannan*, together with tannins from the green peel, contribute to this action, while also providing antibacterial and antifungal properties that reduce biocorrosion (Benzidia et al., 2019, 2023; Mahmoud et al., 2025). Extracts from *Aloe saponaria* have also been tested with comparable results, although with slight colour alteration, which can be mitigated by localised brush applications (Argyropoulos et al., 2021; Benzidia et al., 2023).

The seed extract of *Opuntia ficus indica* has achieved inhibition efficiencies close to 99% on copper, bronze and even iron, due to its phenolic compounds, flavonoids and polysaccharides that generate antioxidant films. Its seed oil, rich in unsaturated fatty acids and tocopherols, provides a hydrophobic barrier against corrosion (Hammouch et al., 2007; Zappa, 2017).

Other notable examples include *olive leaf extract* (Olea europaea), rich in oleuropein, with efficiencies close to 90% in copper under neutral and alkaline conditions, though less effective at high temperatures (Rahal et al., 2016). and *Robinia pseudoacacia*, whose fruits contain sugars and organic acids that form uniform layers acting as mixed inhibitors. At high concentrations, however, fungal growth has been observed, which may compromise long-term stability (Pourzarghan & Fazeli-Nasab, 2021).

Extracts from *papaya, camellia (Camellia sinensis), passion fruit (Passiflora edulis), longan (Dimocarpus longan), sugarcane (Saccharum officinarum), common myrtle (Myrtus communis)* and *jatropha (Jatropha curcas)* have also been tested, achieving inhibition efficiencies between 86% and 98% in acidic media, generally acting through physicochemical adsorption and protective film formation (L. Cao, 2022; Dahmani et al., 2022; Elshahawi et al., 2022; Gao et al., 2021; Tan et al., 2021, 2022).

Among aromatic extracts, *thyme* (Thymus vulgaris) has been widely studied as an anodic inhibitor in bronze under simulated acid rain, with efficiencies above 90% due to the adsorption of phenolic compounds (Fouda et al., 2014; Gonzalez-Rodriguez et al., 2022). *Propolis*, rich in hydroxyl and carbonyl groups, has also been evaluated as an effective anodic inhibitor in slightly acidic solutions and simulated acid rain, reducing both uniform and localised corrosion, although not eliminating it entirely (Grudić et al., 2018; Larios-Galvez et al., 2017; Varvara et al., 2017). Finally, *laurel* (Laurus nobilis) aqueous extracts have shown limited efficiency on bronze with chloride patinas, acting as mixed inhibitors through compounds such as α-terpinene (Chaabani et al., 2017).

8.5.4.2 Amino acids and derivatives

Among amino acids, *L-cysteine* has been one of the most studied as a sustainable alternative to BTA. Its ability to chemically bind to the metal surface and oxidise to cystine helps stabilise copper ions, although it may cause surface darkening when applied in prolonged immersion (Argyropoulos et al., 2021; Berthon, 1995). *Alanine*, by contrast, is less aggressive and acts selectively on corrosion compounds such as brochantite, while preserving stable layers like cuprite and tenorite (Amino Acids Guide, 2024; ChemSrc, 2024; Gaspar et al., 2013; Haynes, 2017).

N-acetylcysteine (NAC), derived from a pharmaceutical product, has also shown high inhibition efficiencies (above 85%) as a cathodic inhibitor, combining both physical adsorption and chemical bonding to the surface (El-Hafez & Badawy, 2013; D.-Q. Zhang et al., 2008).

8.5.4.3 Reused compounds

Recent studies have tested expired antibiotics as green inhibitors, including amoxicillin, ciprofloxacin, doxycycline and streptomycin. These compounds adsorb onto the metal surface through functional groups $–NH_2$, –COOH, C=O and –SH, forming protective films with inhibition efficiencies ranging from 30% to 70%, with doxycycline being the most effective (Rotaru et al., 2014; Shamnamol et al., 2020).

8.5.4.4 Biopolymers and natural gums

Chitosan has been tested both as an inhibitor and as a removable transparent coating, achieving efficiencies up to 90% through adsorption of amino and hydroxyl groups. Combined with molecules such as cysteine or BTA, it provides synergistic effects, enhancing protection without altering the bronze's appearance (El Mouaden et al., 2018; El-Haddad, 2013; C. Giuliani et al., 2018; Jmiai et al., 2017; Messina et al., 2021; Montemor, 2016).

Natural gums, such as guar gum modified with AMPSA, have reached inhibition efficiencies close to 95% in NaCl solutions, acting through hydroxyl and carboxyl adsorption (Korniy et al., 2023; Peter et al., 2015; Vaidya et al., 2022). Other gums, such as arabic and xanthan, have been mainly studied on steel but share similar mechanisms applicable to copper alloys.

8.5.4.5 Hybrid and nanostructured coatings

Smart coatings have been developed to encapsulate inhibitors, such as halloysite nanotubes containing BTA or layered double hydroxides loaded with MBT, which reduce the direct release of toxic compounds while maintaining protective capacity (Casaletto et al., 2016; Pellis, 2025; Pellis et al., 2023, 2024; Salzano de Luna et al., 2018). Acrylic resins modified with alternative inhibitors such as MPT and EDTA have also been tested, representing intermediate strategies between efficiency and sustainability.

In summary, sustainable inhibitors represent a diverse set of alternatives that can reduce reliance on toxic compounds like BTA while still offering effective protection. Plant extracts, amino acids and biopolymers emerge as the most promising options due to their renewable origin and relatively low toxicity. Reused pharmaceuticals and hybrid coatings, while not strictly "green", provide complementary strategies that extend the conservation

toolbox by reducing waste and minimising the environmental impact of traditional practices. The comparative characteristics are presented in Table 8.7.

Table 8.7 - Sustainable inhibitors for bronze conservation: comparative overview

Substance / Family	Nature	Applications / Properties	Limitations / Notes
Plant extracts & oils (Aloe vera, Opuntia, olive leaf, thyme, propolis, laurel, etc.)	Polyphenols, flavonoids, polysaccharides, essential oils	High inhibition (up to 90–99%) in saline/acidic media; protective antioxidant films; antibacterial/antifungal effects	Possible colour changes; fungal growth in some cases (Robinia); reduced efficiency at high temperatures (olive)
Amino acids & derivatives (L-cysteine, alanine, NAC)	Natural compounds with $–NH_2$, –COOH, –SH groups	Selective action on copper corrosion; efficiencies >85%; compatible with sensitive patinas	Darkening after prolonged immersion (cysteine); variable activity depending on the compound
Reused pharmaceuticals (expired antibiotics: doxycycline, ciprofloxacin, etc.)	Complex molecules with multiple functional groups	Adsorption forms protective films; efficiencies 30–70%; re-use concept adds sustainability value	Limited efficiency compared with traditional inhibitors; ethical and availability concerns
Biopolymers (Chitosan)	Natural polysaccharide with amino and hydroxyl groups	Transparent removable coatings; up to 90% efficiency; synergistic effects with cysteine or BTA	May form visible films; requires optimisation of formulations
Natural gums (guar, arabic, xanthan)	Plant-derived polysaccharides	Guar gum + AMPSA reaches ~95% inhibition; act by hydroxyl/carboxyl adsorption	Mainly tested on steel; limited direct data for bronze
Hybrid / nanostructured coatings (halloysite nanotubes, LDH, modified resins)	Carriers embedding inhibitors (BTA, MBT, MPT, EDTA)	Controlled release; reduced environmental impact; maintain polymer barrier properties	Not fully 'green'; some systems still depend on traditional inhibitors

Sources: Data adapted from Argyropoulos et al., 2021; Benzidia et al., 2019, 2023; Berthon, 1995; Casaletto et al., 2016; Chaabani et al., 2017; Dahmani et al., 2022; El-Haddad, 2013; El-Hafez & Badawy, 2013; El Mouaden et al., 2018; Elshahawi et al., 2022; Fouda et al., 2014; Gao et al., 2021; Gaspar et al., 2013; C. Giuliani et al., 2018; Gonzalez-Rodriguez et al., 2022; Grudić et al., 2018; Hammouch et al., 2007; Haynes,

2017; Jmiai et al., 2017; Larios-Galvez et al., 2017; Korniy et al., 2023; L. Cao, 2022; Mahmoud et al., 2025; Messina et al., 2021; Montemor, 2016; Pellis, 2025; Pellis et al., 2023, 2024; Peter et al., 2015; Pourzarghan & Fazeli-Nasab, 2021; Rahal et al., 2016; Rotaru et al., 2014; Salzano de Luna et al., 2018; Shamnamol et al., 2020; Tan et al., 2021, 2022; Vaidya et al., 2022; Varvara et al., 2017; Zappa, 2017; Zhang et al., 2008

8.6 FINAL REMARKS ON CHAPTER 8

The analysis carried out in this chapter confirms that the conservation of bronze sculptures is a field in constant evolution, where long-established techniques converge with the innovations brought by scientific research. The findings highlight the need to balance the preservation of the material and aesthetic integrity of the works with the introduction of approaches that are increasingly sustainable and environmentally responsible.

First, diagnosis has been shown to be a decisive phase. Careful observation, the use of non-invasive methods, and the support of analytical techniques provide a solid basis for conservation decisions, reducing the risk of unnecessary or inappropriate interventions. In this regard, the reports developed by the National Laboratory for Civil Engineering (LNEC) have demonstrated that rigorous scientific study can decisively guide whether an intervention should be carried out or, alternatively, whether a stable state of preservation should be maintained.

Second, the chapter has reviewed the main treatment methodologies, ranging from mechanical, chemical and laser cleaning to the application of inhibitors and protective coatings. It has been emphasised that no technique is entirely neutral or risk-free: all require appropriate calibration, preliminary testing, and ethical evaluation that considers the material and aesthetic history of each work. The diversity of available options reflects both the complexity of corrosion processes and the variety of contexts in which sculptures are situated, whether in museums or in outdoor urban environments.

Finally, the central role of sustainability in contemporary practice has been underlined. The emergence of alternatives based on biopolymers, plant extracts, amino acids or low-impact solvents responds to a growing professional awareness of the risks associated with traditional compounds such as benzotriazole or EDTA. Although many of these products are still at an experimental stage, their development opens promising prospects for the adoption of safer methods that are more compatible with the long-term conservation of metallic heritage.

Taken together, this chapter demonstrates that the conservation of bronze sculptures requires an integrated vision: rigorous diagnosis, careful selection of treatment methods, and openness to innovative solutions that guarantee both technical effectiveness and future sustainability. This approach not only ensures the transmission of artworks to future generations but also aligns the discipline with the ethical and environmental challenges of our time.

CONCLUDING REMARKS AND FUTURE CHALLENGES

This work constitutes the first systematic approach to the material study of the bronze sculptures of António Soares dos Reis, with the aim of contributing both to the knowledge and the preservation of his legacy. The research has integrated historical survey, scientific analysis and reflection on conservation practice. It has documented the context of production and the institutional initiatives that promoted the casting of his work in bronze, while also generating new data on alloy composition and corrosion processes. In this intersection of perspectives, it offers a reference base previously non-existent in the Portuguese context.

Although no conservation-restoration interventions were carried out on the sculptures, the results obtained through instrumental analysis have allowed significant conclusions to be drawn about their state of preservation. The characterisation of the alloys revealed a clear difference between the sculptures cast during the artist's lifetime in the 19th century and the official replicas produced in the mid-20th century. The former present a higher tin content in their composition, while the latter are characterised by a notable reduction of this element, in some cases almost absent, in favour of copper alloys containing small proportions of zinc and lead. These variations in foundry practices influence the behaviour of the works in relation to corrosion processes and require preservation strategies adapted to each group and its specific technical framework.

The historical dimension proves inseparable from the scientific analysis. Archival research made it possible to understand why official replicas in bronze exist: they were promoted by academic and museological institutions as a response to the fragility of a legacy preserved mainly in plaster and terracotta. This historical framework explains the need to characterise

today the alloys and corrosion processes of these replicas, as they became the medium through which the sculptor's work was transmitted. Without this perspective, instrumental analysis would remain disconnected from the patrimonial reality that gives it meaning.

On the scientific level, this work aims to make a significant contribution to the knowledge available on the composition of bronze sculptures and corrosion processes in Portugal. Before this study there were no systematic investigations applied to the material knowledge of Soares dos Reis's bronzes, nor a consolidated corpus on alloys and alteration products in Portuguese bronze sculpture more broadly. The results obtained through characterisation techniques enrich the material understanding of the works analysed and represent a step forward in the scientific study of bronze sculpture produced in Portugal. At the same time, they provide a reference framework that can be expanded in future research in the fields of conservation and sculptural heritage.

It is also important to note the margins this research leaves open. The work focused on a defined group of bronze sculptures by Soares dos Reis, which provides a foundation that does not aim to exhaust the study of Portuguese sculpture of the period. Likewise, although instrumental analysis allowed progress in understanding the state of preservation of the pieces, other factors remain to be explored that may influence alteration processes, such as the action of microorganisms or the prolonged interaction with specific atmospheric pollutants. Conservation-restoration interventions were not addressed, so the conclusions remain within the scope of diagnosis and analytical interpretation. These limitations do not diminish the scope of the results but rather indicate possible directions for continuity in future research.

Looking ahead, this work highlights the need to continue both historical and contemporary research into the art foundry profession, with particular attention to its current situation in Portugal, and in comparison, with other European contexts. This approach will make it possible to understand not only the past evolution of workshops and their practices but also the challenges and opportunities faced by art foundries today in a globalised context.

It is essential to deepen the study of corrosion factors in relation to the specific climatic and geographical conditions of each region of Portugal. Despite being a relatively small country,

it presents a remarkable diversity of environments, ranging from coastal areas exposed to salinity to urban centres with high levels of atmospheric pollution, and inland regions subject to marked variations in humidity and temperature. This heterogeneity directly conditions the evolution of patinas and alteration products in bronze sculptures and explains why uniform conservation solutions cannot be applied across the territory. Progress towards a systematic mapping of corrosion processes, linking analytical data with local environmental parameters, thus emerges as one of the most important future challenges. This approach will not only allow a better understanding of deterioration dynamics but also anticipate risks and design preventive conservation strategies adapted to each context, strengthening heritage management at the national level.

Another research challenge is the study of bacterial corrosion, in particular that associated with anaerobic bacteria. This phenomenon has been analysed mainly in industrial contexts but has not yet received systematic attention in the artistic field. Its study is especially relevant in sculptures immersed in water, associated with fountain systems, or with very dense corrosion layers that could, in theory, promote the development of such organisms. Although this line of research was foreseen within this work, various administrative and general factors, including the COVID-19 pandemic, prevented it from being developed in a fluid way. Resuming this path in the future will allow a broader understanding of deterioration processes in bronze sculptures, incorporating biological dimensions that have so far been little explored and that represent an emerging field in the conservation of metallic heritage.

The results of the international questionnaire included in this work demonstrate, in turn, the growing importance that professionals attribute to sustainability in the conservation of bronze sculptures. Although the measures adopted are still concentrated on operational aspects such as the substitution of solvents or the responsible management of waste, there is a clear will to move towards safer and more environmentally respectful practices. This panorama resonates with recent research that has begun to explore alternative compounds such as biopolymers, amino acids, plant extracts and low-impact solvents. Testing their effectiveness on bronze sculptures, both under laboratory conditions and in controlled

applications on heritage objects, constitutes a necessary line of research. In this sense, detailed knowledge of the methods currently in use is essential not only to evaluate their technical performance but also to inform the transition towards strategies that combine effectiveness with sustainability, in response to the contemporary challenges of conservation and heritage care.

Taken together, this work has shown how the combination of scientific analysis and historical study allows a deeper understanding of António Soares dos Reis's bronze sculptures and, by extension, of the art foundry profession in Portugal. The results obtained contribute to improving the information available on alloy composition and corrosion processes, while also providing documentation on the history and context of their production. Beyond the advances achieved, what is presented here should be understood as a starting point for future research that may broaden and complement these perspectives, whether in the historical, technical or methodological domains. Ultimately, the research seeks to contribute to ensuring that the preservation of Soares dos Reis's legacy, and with it Portuguese bronze sculpture, is carried out in a more informed and responsible way.

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APPENDIX

APPENDIX A SUPPLEMENTARY MATERIAL FOR CHAPTER 3

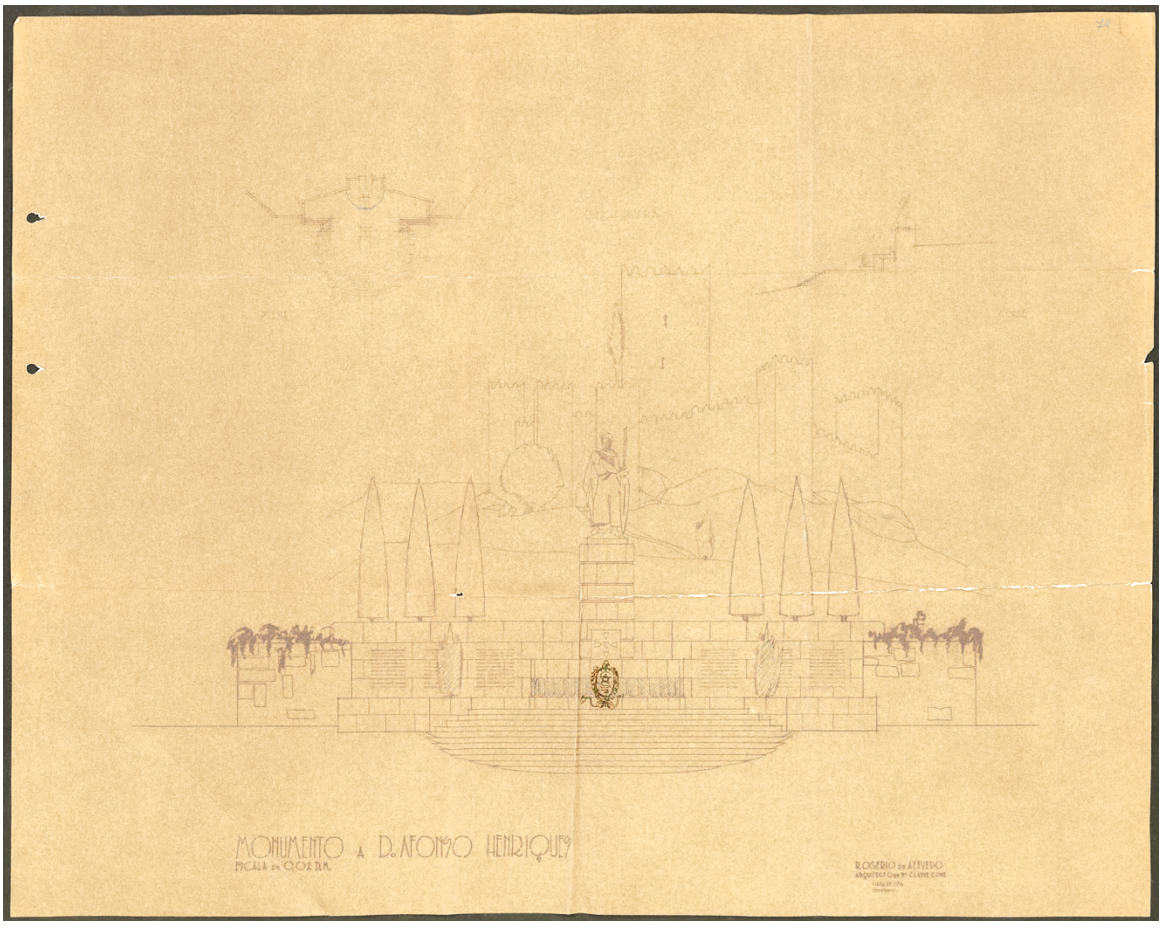
APPENDIX A.1 MONUMENT TO KING AFONSO HENRIQUES IN ITS SECOND LOCATION AT LARGO DO TOURAL, GUIMARÃES.

Obtained from *Gazeta dos Caminhos de Ferro*, no. 1174, 16 November 1936. Digitised by the Municipal Newspaper Library of Lisbon.



APPENDIX A.2 DESIGN BY ARCHITECT ROGÉRIO DE AZEVEDO FOR THE RELOCATION OF THE MONUMENT TO KING AFONSO HENRIQUES, IN FRONT OF THE PALACE OF THE DUKES OF BRAGANÇA, GUIMARÃES (1941).

Title: PT-AMAP-MGMR-ADP-CMGMR-M-2151_m0010. Image courtesy of the Arquivo Municipal Alfredo Pimenta.



APPENDIX A.3 CORRESPONDENCE FROM SOARES DOS REIS TO JOSÉ ANTÓNIO GASPAR.

Obtained from Figueiredo & Valente (1942), *Correspondência inédita de Soares dos Reis*. Porto: Revista Museu, Vol. I, p. 25.

[Original]

"*V.N. de Gaya 18 de Maio de 1884*

Amº Gaspar

Escrevo-lhe esta mas não é para lhe responder á sua (sem data) ultima porque n'este momento não se trata de chalaça mas de cousa seria. O caso é o seguinte: em Guimarães vão levantar uma estatua á memoria do fundador na monarchia e mandaram-me perguntar se com 6 contos de reis se podia fazer toda a obra, isto é, estatua e pedestal, e quer, pode ou convem-lhe fazer o projecto da cousa ficando associado comigo até á sua conclusão? Responda-me, faça-me esse favor, sem demora sim ou não ou então o que é que lhe conviria.

Lembranças a todos

Seu Amº

A. S. dos Reis."

[English Translation]

Vila Nova de Gaia 18th of May 1884

My friend Gaspar,

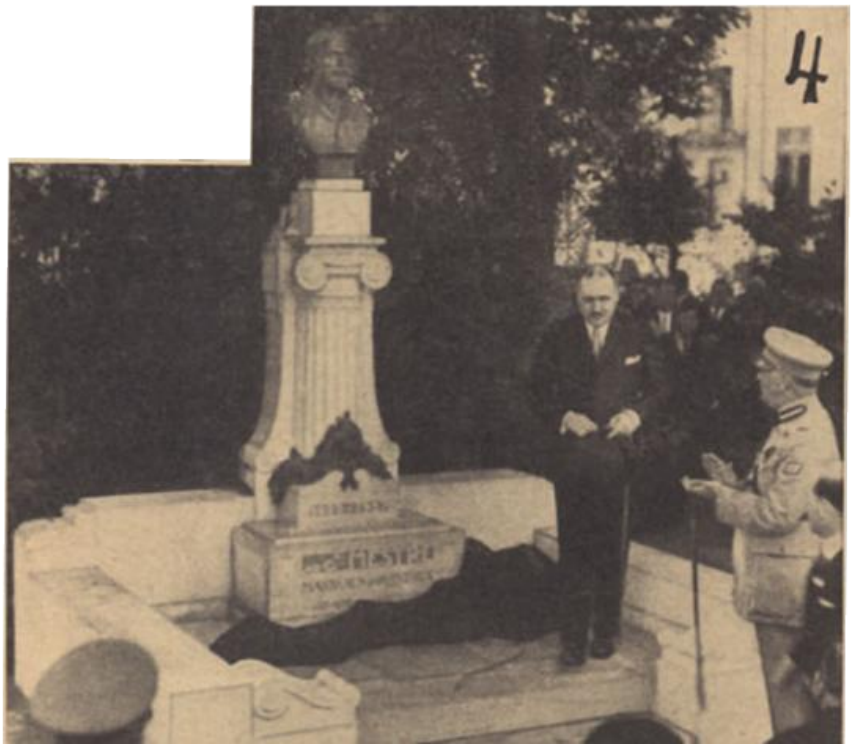
I am writing to you, but it's not in response to your last letter (undated). This one is not about jokes; it concerns a serious matter. The case is as follows: in Guimarães, they are planning to erect a statue in memory of the founder of the monarchy, and they asked me if the entire work, including the statue and pedestal, could be done with *6 contos de reis*. Additionally, they want to know if you can, want to, or should be willing to design the project and be associated with me until its completion. Please respond promptly with a yes or no, or let me know what would suit you.

Greetings to all,

Your friend,
A.S. dos Reis

APPENDIX A.4 INAUGURATION OF THE BUST OF MARQUES DE OLIVEIRA, 11 APRIL 1929

Obtained from *Ilustração*, 1 May 1929, p. 12.



APPENDIX A.5 CORRESPONDENCE RECEIVED BY THE MNSR IN 1933: INTEREST OF THE STONEMASON MOREIRA RATO IN THE SALE OF PLASTER MODELS BY SOARES DOS REIS

Obtained from *Correspondência Recebida 1938. Archive MNSR*

[Original]

Antonio Moreira Rato y F.^{os} L.^{da}
CASA FUNDADA EN 1840

Lisboa, 7 de Novembro de 1933

Exm^{o} Snr. Director do
MUSEU "SOARES DOS REIS"
PORTO

Tendo em nossa oficina, alguns modelos, em gêsso, assinados pelo insigne artista Soares dos Reis, vimos informar V. Ex^{a} que, no caso de interessar, poderiamos entrar em trasacções com os mesmos.

Agradecendo as noticias de V. Ex^{a} sobre o asunto, somos com estima e consideração,

De V. Ex^{a}
Attos. Vnrs. E Obrgs.

(Assinatura de António Moreira Rato)

[English translation]

Antonio Moreira Rato & Sons, Ltd.
HOUSE FOUNDED IN 1840

Lisbon, 7 November 1933

To His Excellency the Director of the
MUSEU SOARES DOS REIS
PORTO

Sir,

Having in our workshop several plaster models signed by the distinguished artist Soares dos Reis, we wish to inform Your Excellency that, should there be any interest, we would be willing to enter into negotiations regarding them.

Awaiting Your Excellency's reply on the matter, we remain, with esteem and consideration,

Your most attentive and obliged servants,

(Signed: António Moreira Rato)

APPENDIX A.6 CORRESPONDENCE SENT BY ANTÓNIO MOREIRA RATO & SONS TO THE MNSR IN 1938: ACKNOWLEDGEMENT OF RECEIPT AND DISPATCH OF PHOTOGRAPHS OF PLASTER STATUES BY SOARES DOS REIS

Obtained from *Correspondência recebida 1938, Lº 3º, Nº 32, Arquivo MNSR.*

Exmos. Snrs. Antonio Moreira Rato & Filhos, Lda
Avenida 24 de Julho
Lisboa

Em referência ao ofício de V. Ex.ª, de 15 de Março último, tenho a honra de informar, conforme verbalmente já lhes participei, que em princípio muito interessa a este Estabelecimento a aquisição das quatro estatuas em gêsso, originaes de Soares dos Reis, rogando a V. V. Ex.as. o favor de me enviarem com a possível brevidade fotografías e dimensões dos referidos gêsos.

A BEM DA NAÇÃO

Porto e Museu Nacional de Soares dos Reis,
em 12 de Abril de 1938.

O DIRECTOR

[English translation]

No. 33 – No. 32
To Messrs. António Moreira Rato & Sons, Ltd.
Avenida 24 de Julho
Lisbon

In reference to Your Excellency's letter of the 15th of March last, I have the honour to inform you, as I have already communicated verbally, that this Institution is, in principle, very interested in the acquisition of the four plaster statues, originals by Soares dos Reis, and I kindly request that Your Excellencies send me, as soon as possible, photographs and the dimensions of the said plaster works.

FOR THE GOOD OF THE NATION

Porto, Museu Nacional Soares dos Reis

12 April 1938.

THE DIRECTOR

APPENDIX A.7 CORRESPONDENCE SENT BY ANTÓNIO MOREIRA RATO & SONS TO THE MNSR IN 1938: ACKNOWLEDGEMENT OF RECEIPT AND DISPATCH OF PHOTOGRAPHS OF PLASTER STATUES BY SOARES DOS REIS

Obtained from *Correspondência recebida 1938, Docto. 45. April 27, 1938.*

[Original]

Lisboa, 26 de Abril de 1938

Exmº. Snr. Director do
MUSEU SOARES DOS REIS
Porto

Amigo e Snr.

Recebemos a prezada carta de V. Ex.ª n.º 32, de 12 do corrente, que agradecemos e por este correio remetemos, sob registo, as fotografias das 4 esculturas da autoria de Soares dos Reis.

As dimensões dessas esculturas são de 1,40 de altura e 0,44 de base, aproximadamente.

Aguardando as suas prezadas notícias, somos com estima e consideração

De V. Ex.ªAt.ºs Vnrs. Obg.ºs

António Moreira Rato

[English versión]

To His Excellency the Director of the
MUSEU SOARES DOS REIS
Porto

Dear Sir,

We have received Your Excellency's valued letter no. 32 of the 12th of this month, for which we thank you, and by this post we are sending, by registered mail, the photographs of the four sculptures by Soares dos Reis.

The dimensions of these sculptures are approximately 1.40 m in height and 0.44 m at the base.

Awaiting Your Excellency's kind reply, we remain, with esteem and consideration,

Your most attentive and obliged servants,

António Moreira Rato

APPENDIX A.8 CORRESPONDENCE SENT BY THE MNSR TO THE NATIONAL BOARD OF EDUCATION IN 1938: REQUEST FOR THE TRANSFER OF PLASTER STATUETTES BY SOARES DOS REIS

Obtained from: Correspondência recebida 1938. Lº 113, 3ª. Arquivo MNSR

[Original]

Exmo. Snr. Presidente da 6ª Secção da

Junta Nacional da Educação

Lisboa

Tendo Sua Ex.ª o Ministro, por despacho de 30 de Maio último, homologado o parecer favorável da 6ª Secção da Junta Nacional da Educação sobre a aquisição de quatro estatuetas, gêsos originais de Soares dos Reis, transação proposta pela firma Antonio Moreira Rato & F.os, L.da, a este Museu, que a não pôde efectuar, por falta de verba, foram as mesmas estatuetas adquiridas, depois de novamente ouvida a 6ª Secção, por fôrça da alínea b) – artº 2478 do orçamento – Aquisições de utilização permanente – Aquisição de móveis (obras d'arte) de que dispunta o Museu Nacional de Arte Contemporânea, e por isso venho pedir a V. Ex.ª que, em face do nº 8 do § 1º do artº 21 do Regulamento dessa Junta, promova a sua transferência para êste Estabelecimento assim como a de outros trabalhos do mesmo Artista que o referido Museu possa dispensar.

A Bem da Nação

Porto e Museu Nacional de Soares dos Reis,

em 9 de Dezembro de 1938.

[English translation]

To His Excellency the President of the 6th Section of the

National Board of Education

Lisbon

As His Excellency the Minister, by decree of the 30th of May last, approved the favourable opinion of the 6th Section of the National Board of Education regarding the acquisition of four plaster statuettes —original works by Soares dos Reis — proposed to this Museum by the firm António Moreira Rato & Sons, Ltd., which could not be carried out at the time due to lack of funds, those same statuettes were later acquired, after the 6th Section had been heard again, under clause b) – article 2478 of the budget – "Permanent acquisitions – Acquisition of furniture (works of art)" — by the National Museum of Contemporary Art.

For this reason, I now request that Your Excellency, in accordance with No. 8, §1, article 21 of the Regulation of that Board, promote the transfer of the said works to this Institution, as well as of other works by the same artist that the aforementioned Museum may be able to spare.

For the Good of the Nation

Porto, National Museum Soares dos Reis,

9 December 1938.

APPENDIX A.9 LETTER FROM SOARES DOS REIS TO THE DIRECTOR OF THE VIMARANENSE COMMISSION FOR THE MONUMENT TO KING AFONSO HENRIQUES.

Obtained from Arquivo Municipal Alfredo Pimenta, Guimarães, cota 10-27-19-1, doct. 10.

[Original]

"V.N. de Gaya 11 de Junho de 1885

Ex.mo Senhor

Communiquei ao meu collega a observação de V. Ex.ª relativa à modificação da condição de serem pagos 1:000$000 no acto de ser assignado o contrato a tantos eles como eu aceitamos a modificação visto ser de conveniência para a Ex.ma Commissão.

Com referencia ao bronce fornecido pelo governo, lembro a V. Ex.ª que aos fundidores convemlhes sempre fornecer o metal aceitando-o por um prezo relativamente insignificante quando fornecido por quem quer que seja. Alem disso a circunstancia de o governo fornecer o metal obriganos a fundir a estatua no paiz e a regeirtar-nos ao preço que queiram fazer.

E´certo que a nossa intenção é de que o trabalho seja feito entre nós mas queremos [ilegible] liberdade de acção para não vermos explorado e podermos tomar toda a responsabilidade que nos remeta a obra.

Relativamente ao desenho do projecto para a V. Ex.ª o obsequio de m'o mandar o mais breve que pareça ser para se tirarem as copias necessárias. Ao respeito da planta do

referido projecto não é preciso modificar cousa alguma porque se considera sempre completa desde que uma metade é exactamente igual a outra.

No que havera modificações é nos capiteis, mas só se fara na execução e segundo algum dos que ahi [ilegible] por ocasi~åo de assignarmos o contracto.

Guardamo-nos também para antes darmos todas as explicações que a Ex.ma Commissão desejar.

A collocação da primeria pedra podra ter lugar em Dezembro, salo caso de força maior.

Sou com a maior consideração e respeito

De V. Ex.a
Att.to Ven.dor[?]
Antonio Soares dos Reis

[English translation]

Vila Nova de Gaia, 11 June 1885

Most Excellent Sir,

I communicated to my colleague Your Excellency's observation concerning the modification of the condition that 1:000$000 be paid at the signing of the contract, and both he and I accepted the modification, as it was deemed convenient for the Honourable Commission.

With regard to the bronze supplied by the government, I would remind Your Excellency that founders always find it advantageous to provide the metal themselves, accepting it at a relatively insignificant price when it is supplied by whomever it may be. Moreover, the fact that the government supplies the metal obliges us to cast the statue in the country and to submit to the price they may set.

It is true that our intention is for the work to be carried out among ourselves, but we also wish [illegible] freedom of action, so that we may not be exploited and may assume full responsibility for the delivery of the work.

With regard to the design of the project, I beg Your Excellency to be so kind as to send it to me as soon as possible, in order that the necessary copies may be taken. As for the plan of the said project, there is no need to alter anything, as it is always considered complete, since one half is exactly identical to the other.

The modifications will concern the capitals, but these will only be made in the execution, according to one of those [illegible] at the time of signing the contract.

We also reserve the right to provide beforehand any explanations the Honourable Commission may wish.

The laying of the first stone may take place in December, unless prevented by circumstances of force majeure.

With the greatest consideration and respect,

Your Excellency's most attentive servant,

Antonio Soares dos Reis

APPENDIX A.10 BUDGET FOR THE CASTING OF ELEVEN WORKS BY SOARES DOS REIS.

Obtained from the Arquivo Faculdade de Belas Artes do Porto. Correspondência Recebida 1920, Reference number 212. Date: 24 of December 1920.

[Original]

FUNDIÇÃO DE BRONZE D'ARTE
Adelino de Sá Lemos
VILA NOVA DE GAIA

"Ex^{mo} Sr.
Director da Escola de Bellas Artes do Porto.

Satisfacendo o pedido de V. Ex^{a} sobre a fundição em bronce dos trabalhos em gesso de Soares dos Reis, existentes no museu de S. Lazaro, cujos são as estatuas S. Joaquim, S. José, Pescador, uma academia, cinco bustos diferentes; e do medalhão Augusto Candido Ramos, bem como do busto Correia de Barros, que V. Ex conta obter, cumpreme-me propor o preço de 12 contos Esc. 12:000$.

Saude e Fraternidade

Villa Nova de Gaia, 24 de Dezembro 1920

Adelino de Sá Lemos"

[English translation]

FUNDIÇÃO DE BRONZE D'ARTE
Adelino de Sá Lemos
VILA NOVA DE GAIA

"Honourable Director of the School of Fine Arts of Porto,

In compliance with Your Excellency's request concerning the bronze casting of the plaster works by Soares dos Reis, currently held at the São Lázaro Museum, including the statues *São Joaquim*, *São José*, *Pescador*, an *Academia*, five different busts, as well as the medallion of *Augusto Cândido Ramos* and the bust of *Correia de Barros*, which Your Excellency intends to obtain, I hereby propose a price of 12 contos, Esc. 12:000$.

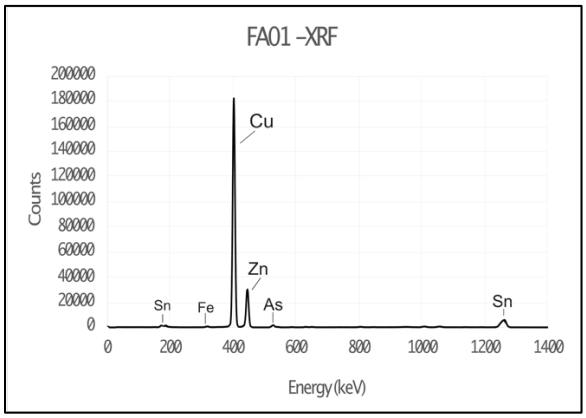
Health and Fraternity,

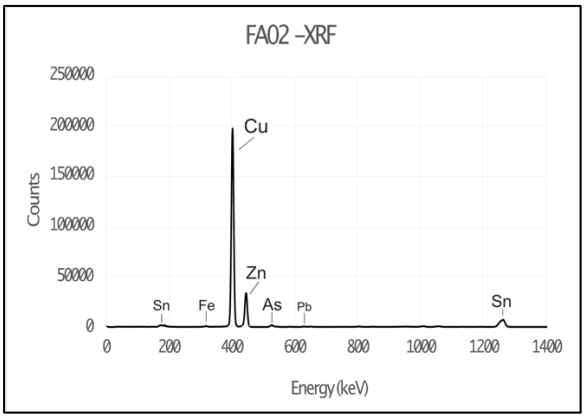
Vila Nova de Gaia, 24th December 1920

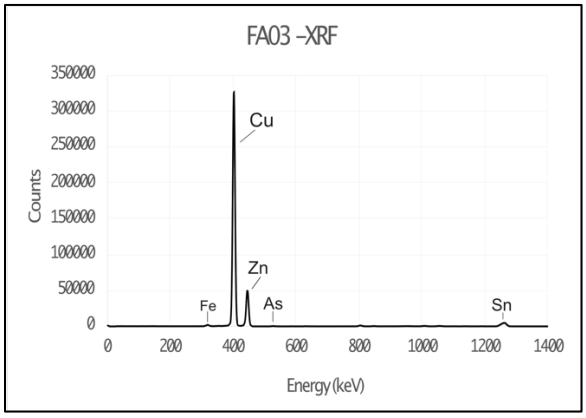
Adelino de Sá Lemos"

APPENDIX B SUPPLEMENTARY MATERIAL FOR CHAPTER 5

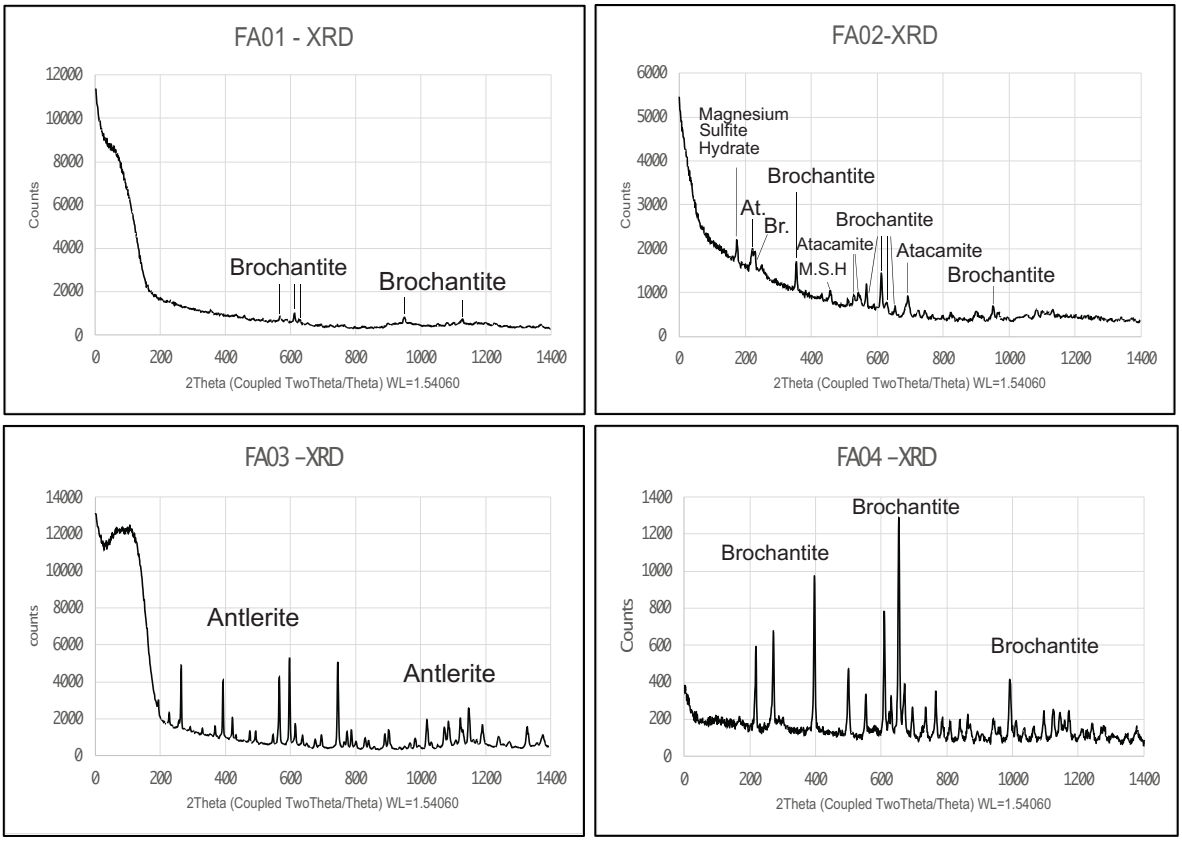
APPENDIX B.1 XRF SPECTRA FROM THE ANALYSIS OF THE *SCULPTURE OF FRANCISCO DE ALMADA E MENDONÇA*



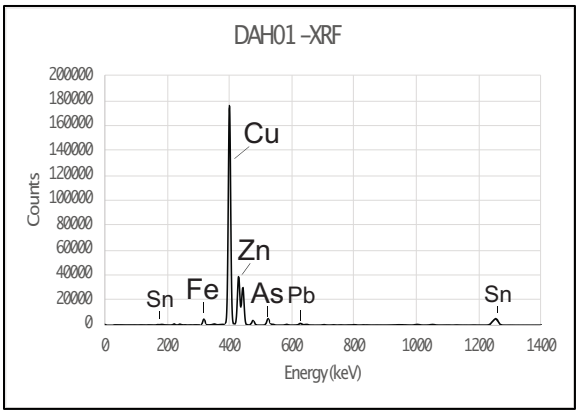


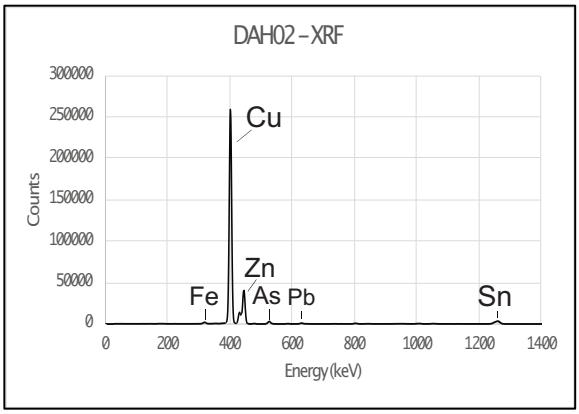


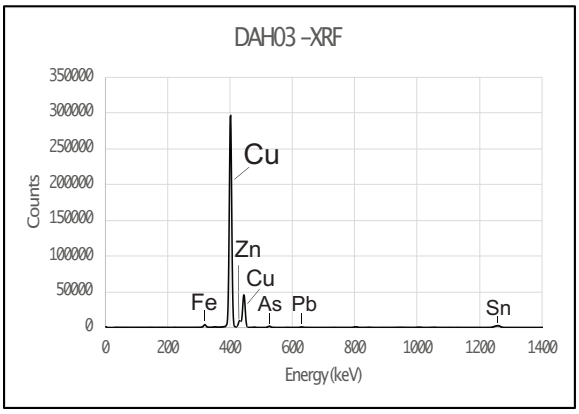
APPENDIX B2 XRD SPECTRA FROM THE ANALYSIS OF THE *SCULPTURE OF FRANCISCO DE ALMADA E MENDONÇA*

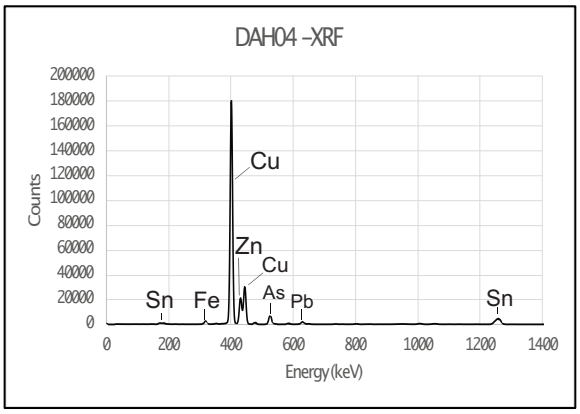


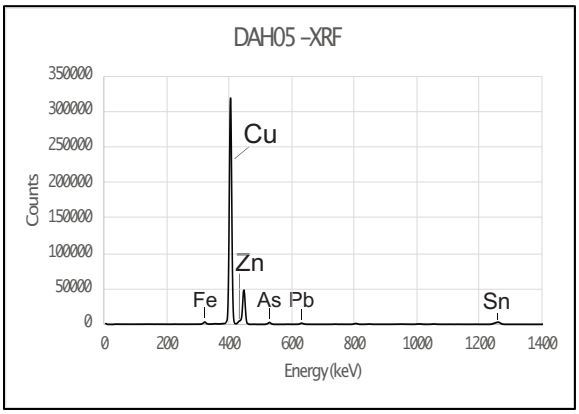
APPENDIX B.3 XRF SPECTRA FROM THE ANALYSIS OF THE STATUE OF *KING AFONSO HENRIQUES*



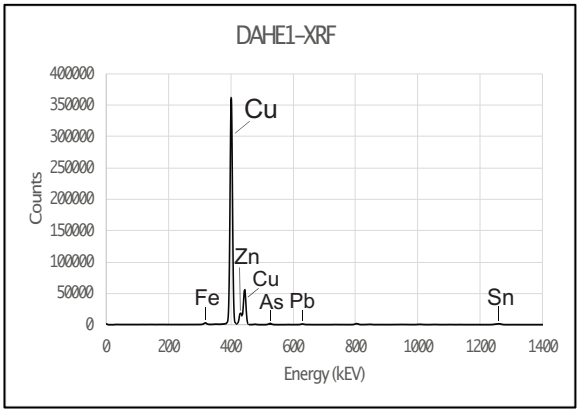


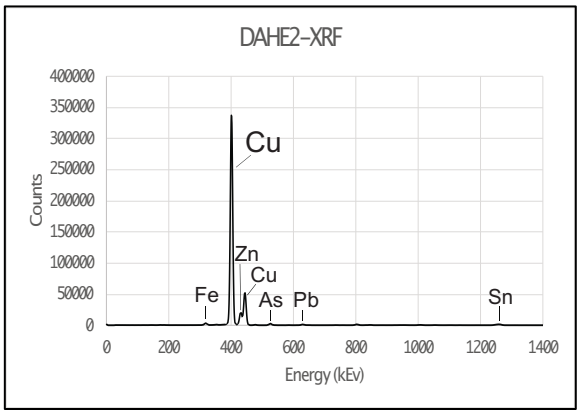


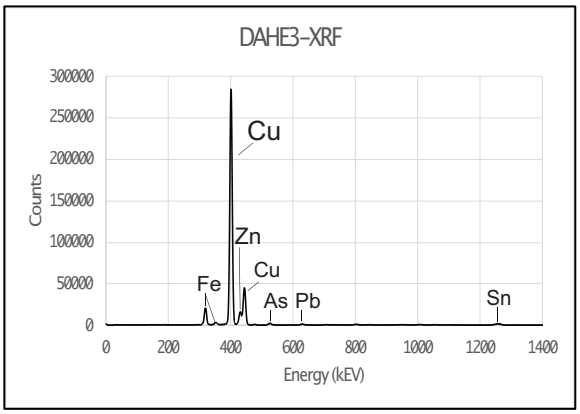


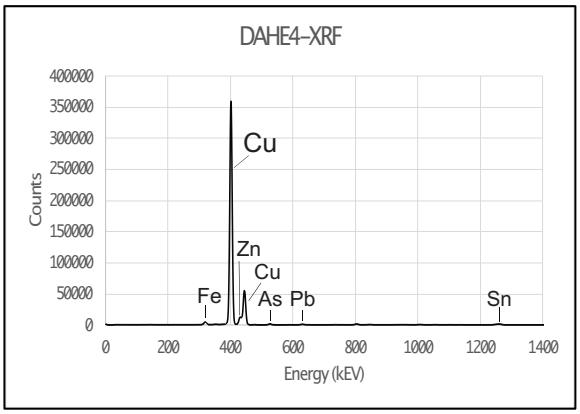


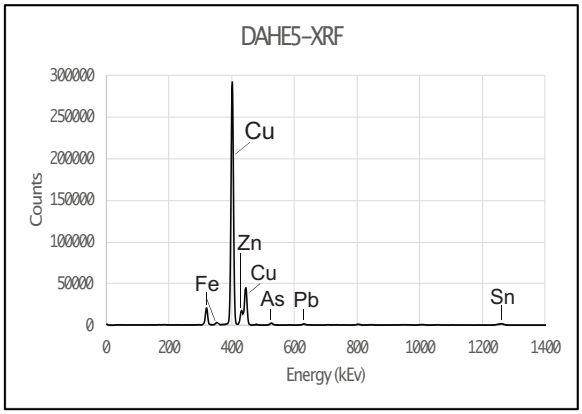
APPENDIX B.4 XRF SPECTRA FROM THE ANALYSIS OF THE SWORD OF *KING AFONSO HENRIQUES*

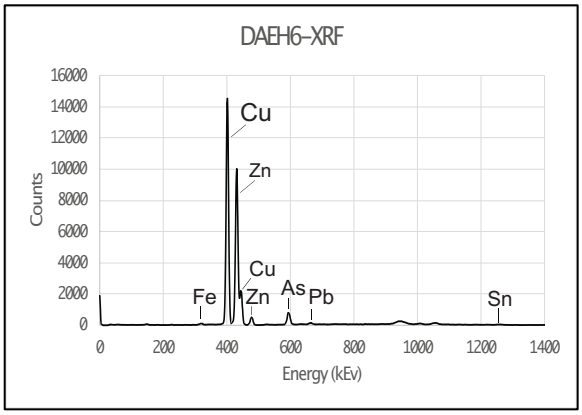


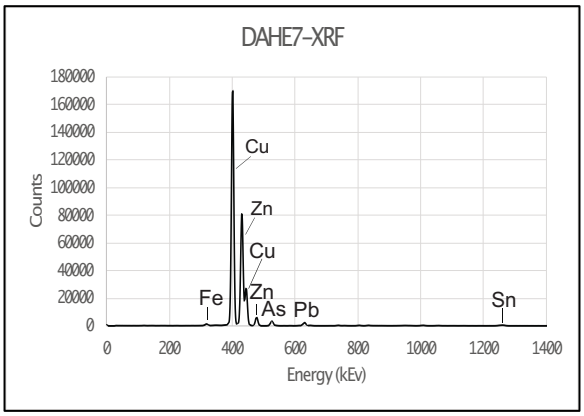


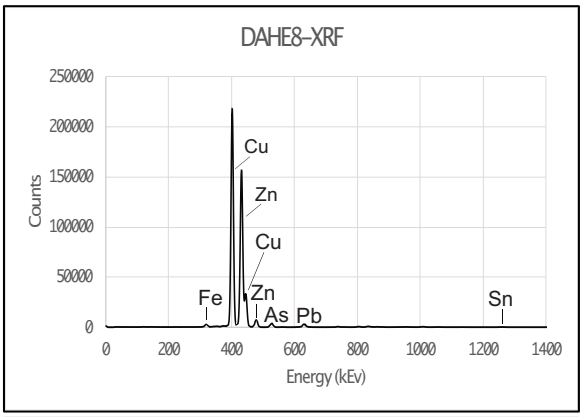


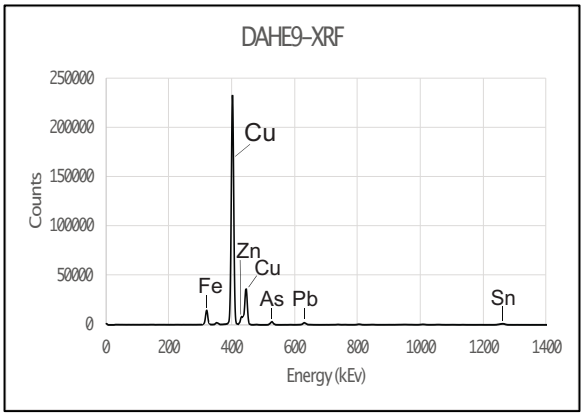


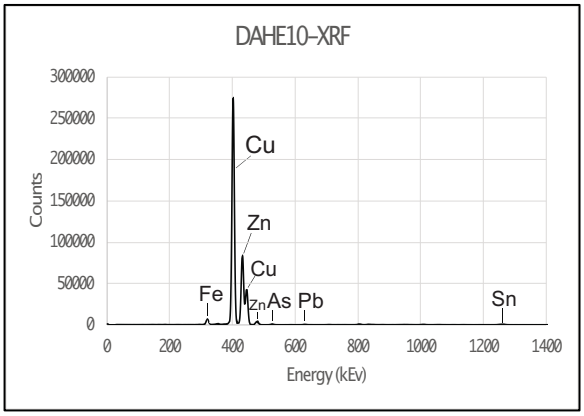


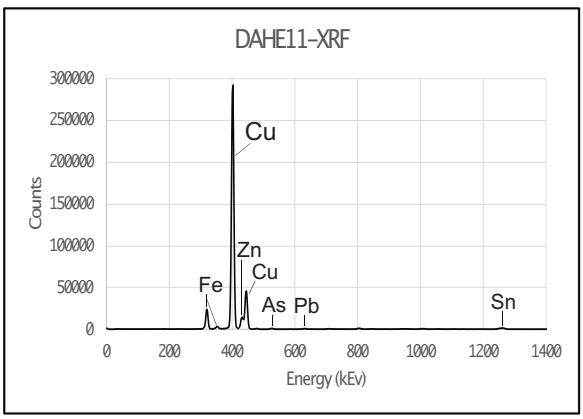


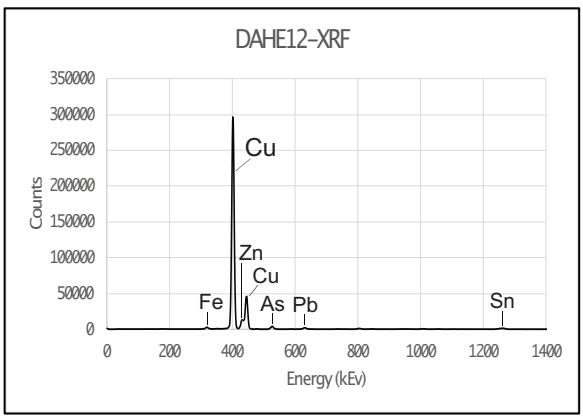

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Cu
Zn
Cu
Zn
As Pb
Sn


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Counts
Energy (kEv)
Fe
Cu
Zn
Cu
Zn
As Pb
Sn

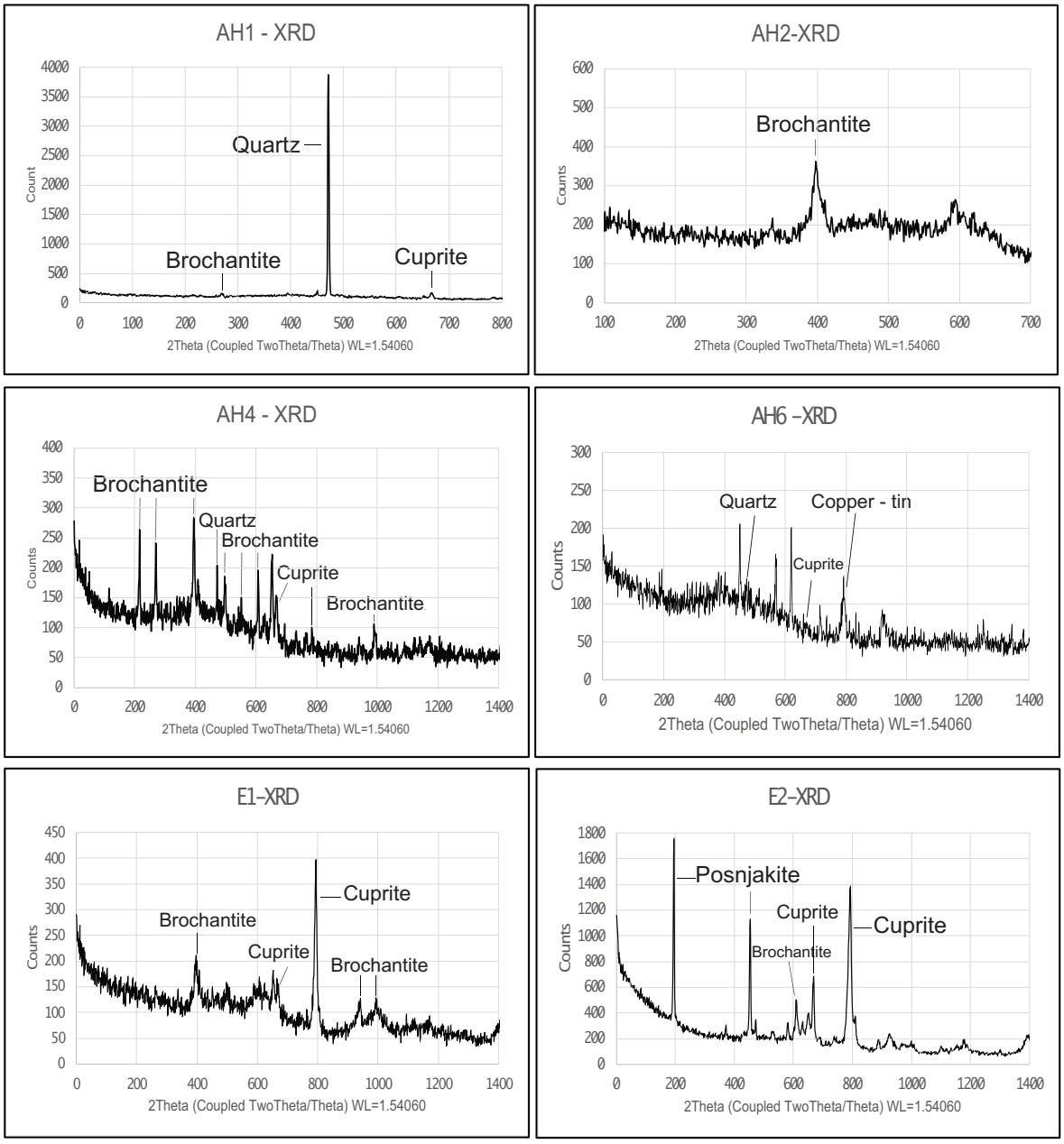

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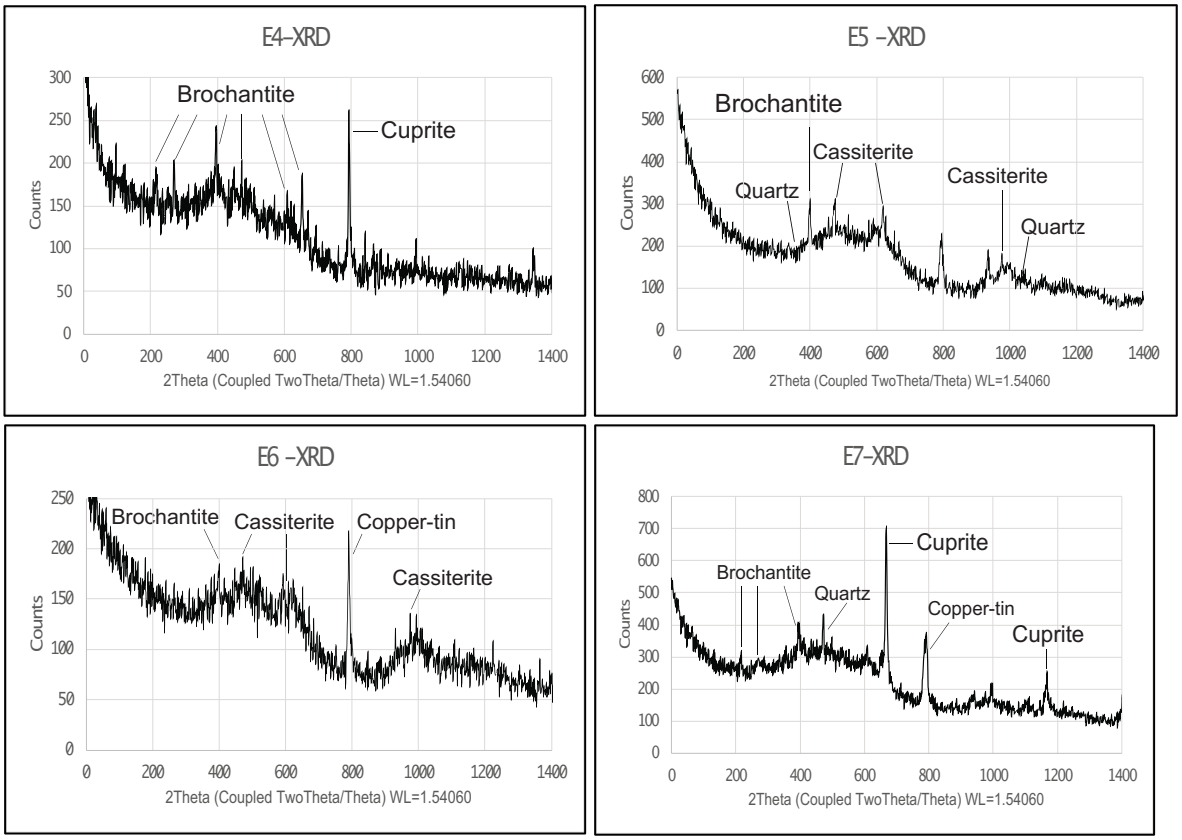

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As Pb
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Energy (kEv)
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As Pb
Sn

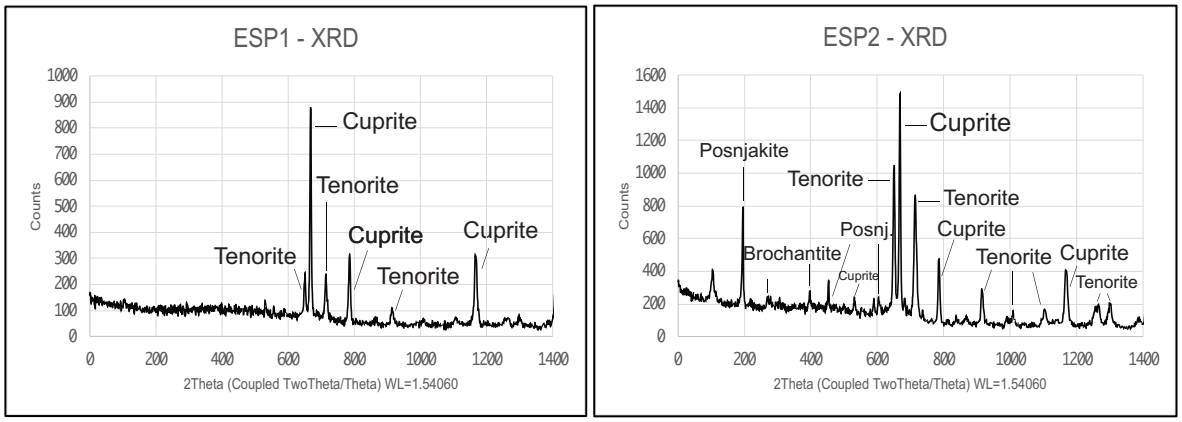

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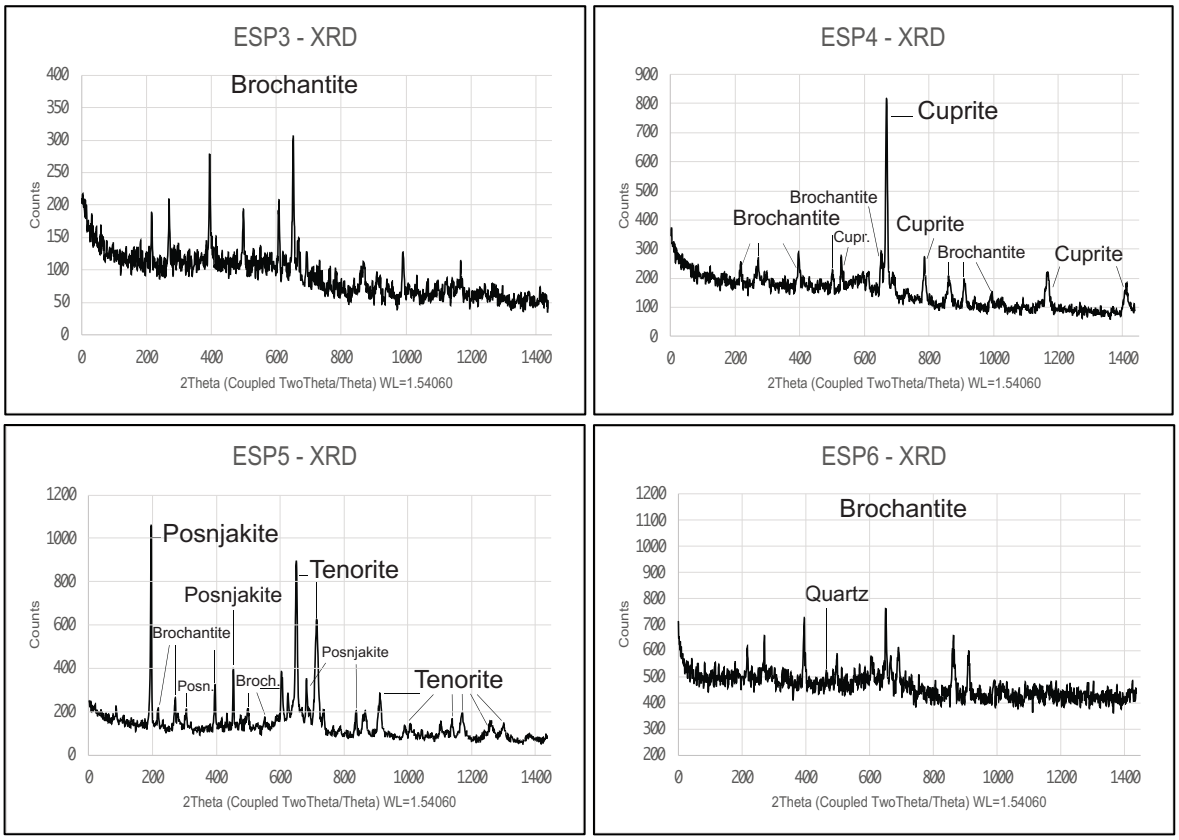
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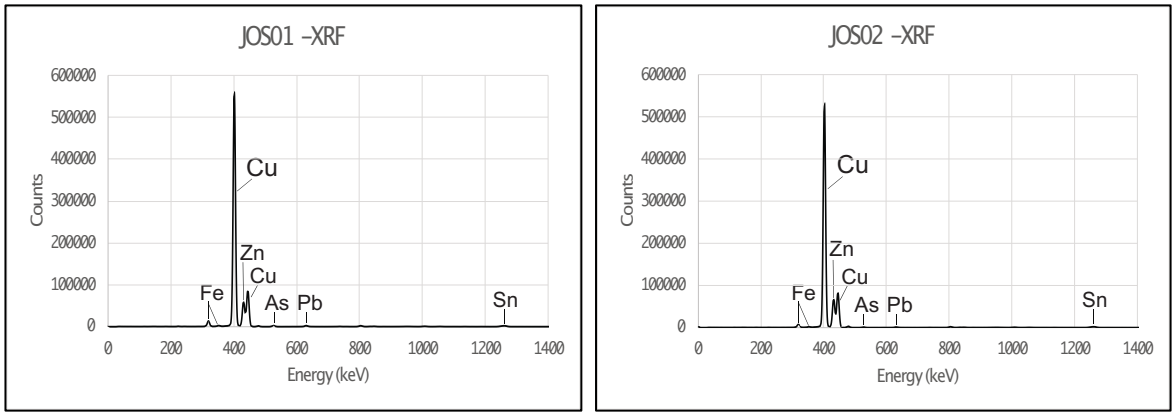


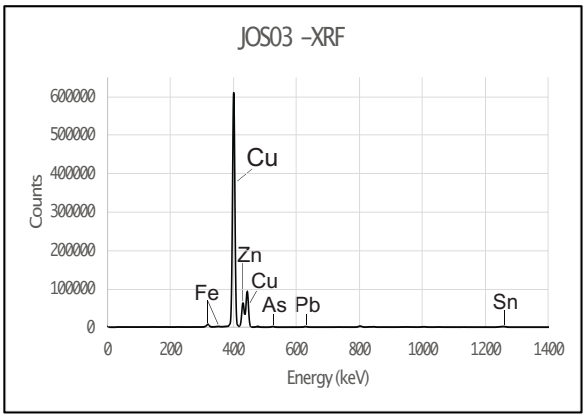
APPENDIX B.6 XRD SPECTRA FROM THE ANALYSIS OF THE SWORD OF *KING AFONSO HENRIQUES*

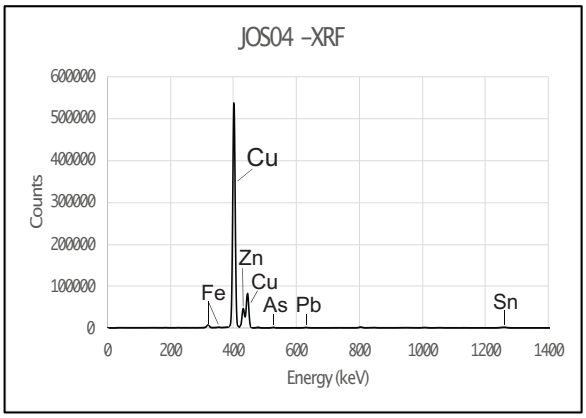




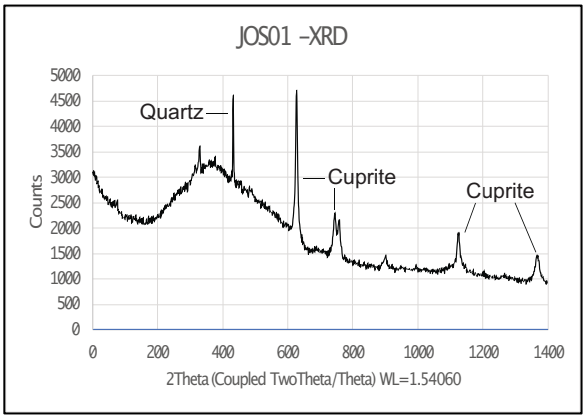
APPENDIX B.7 XRF SPECTRA FROM THE ANALYSIS OF THE SCULPTURE OF *S. JOSÉ*

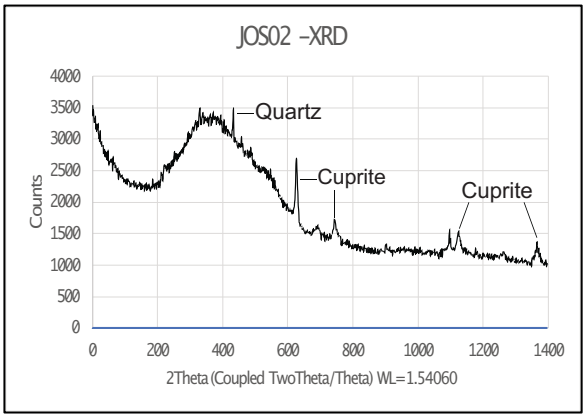




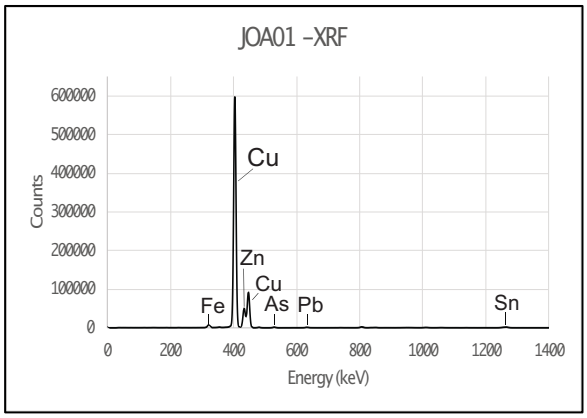


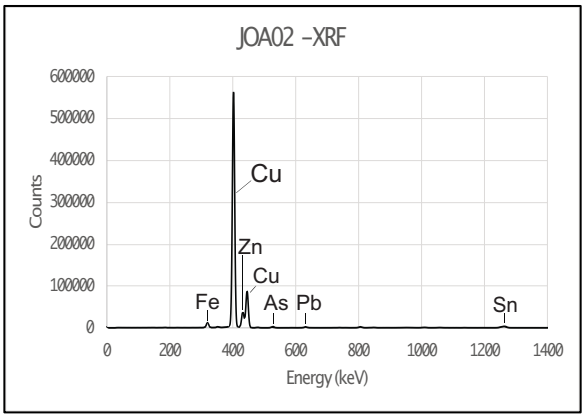
APPENDIX B.8 XRD SPECTRA FROM THE ANALYSIS OF THE SCULPTURE OF *S. JOSÉ*

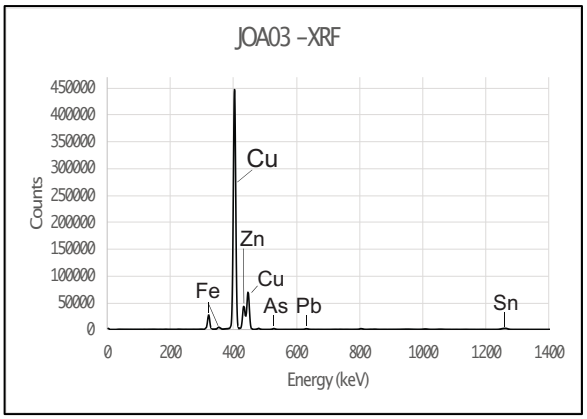




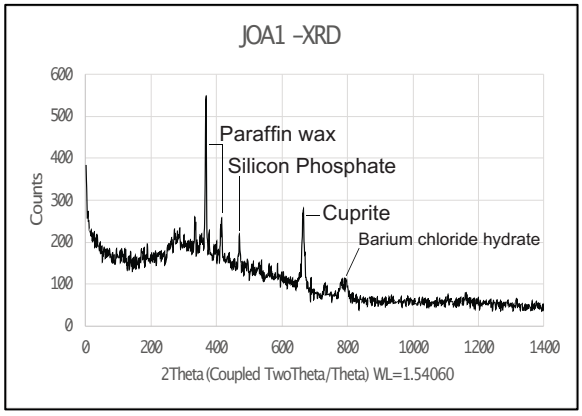
APPENDIX B.9 XRF SPECTRA FROM THE ANALYSIS OF THE SCULPTURE OF *S. JOAQUIM*

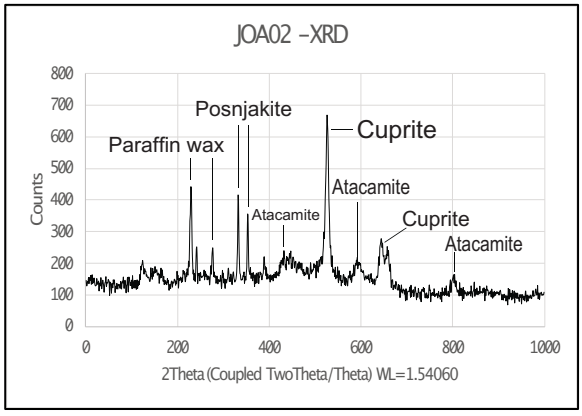




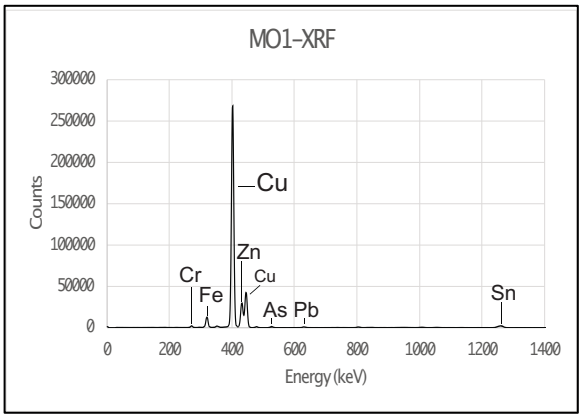


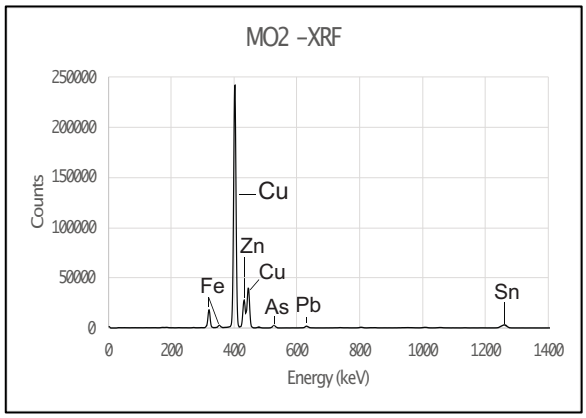
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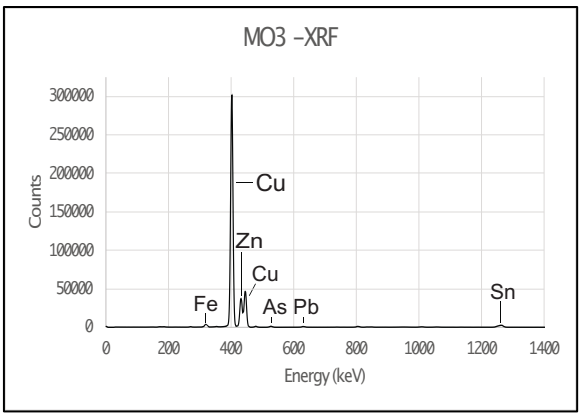


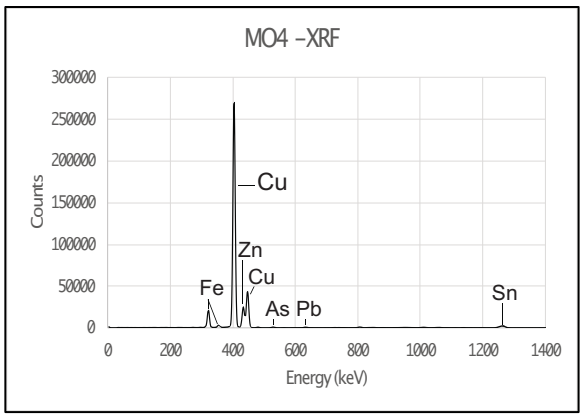


APPENDIX B.11 XRF SPECTRA FROM THE ANALYSIS OF THE BUST OF *JOÃO MARQUES DE OLIVEIRA*

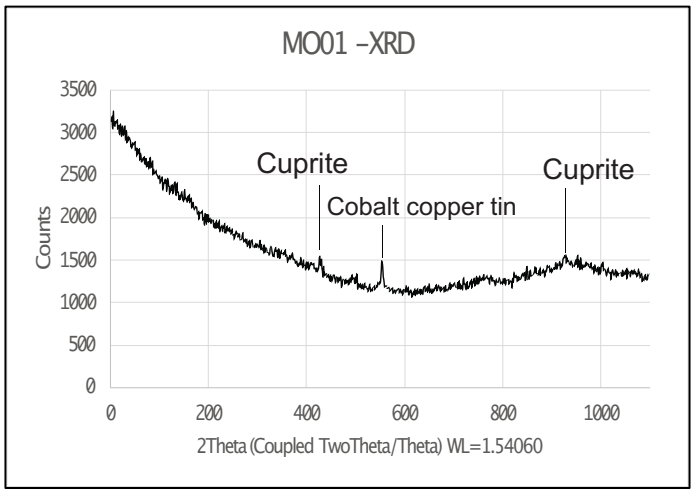




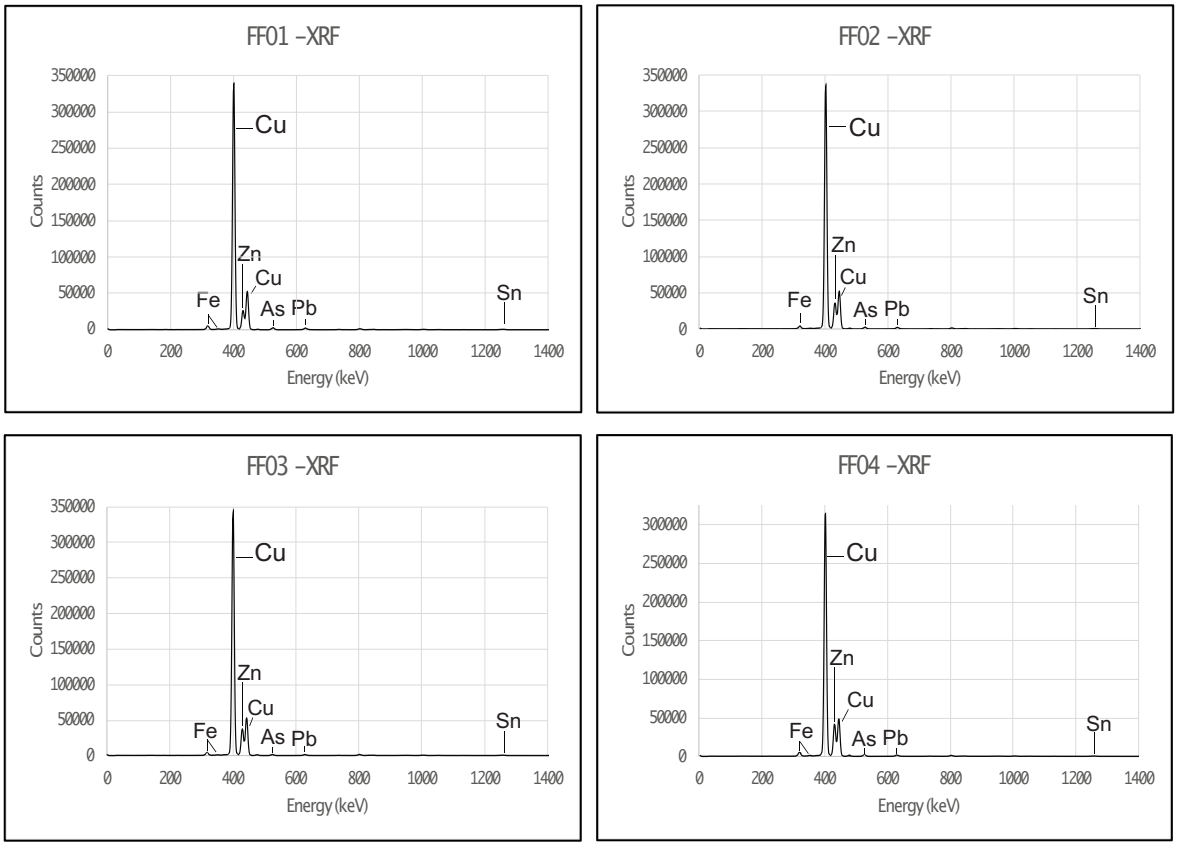




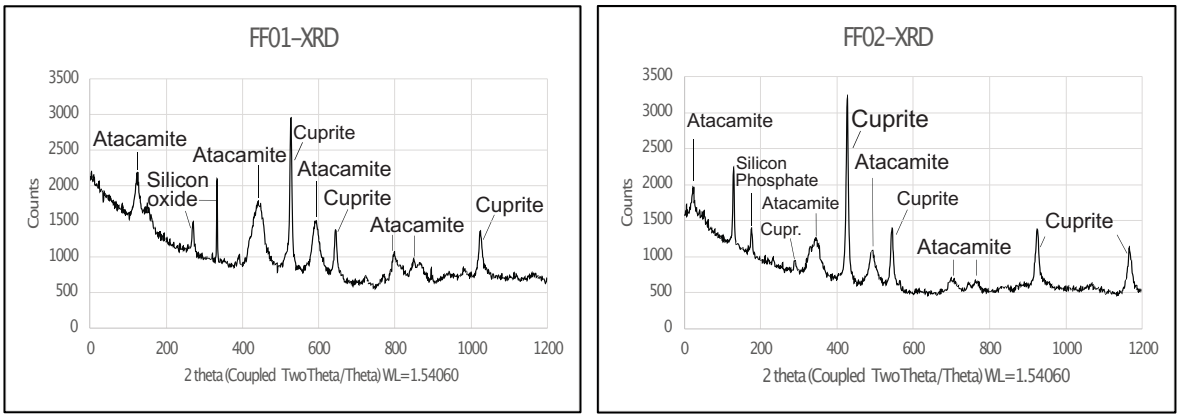
APPENDIX B.12 XRD SPECTRA FROM THE ANALYSIS OF THE BUST OF *JOÃO MARQUES DE OLIVEIRA*



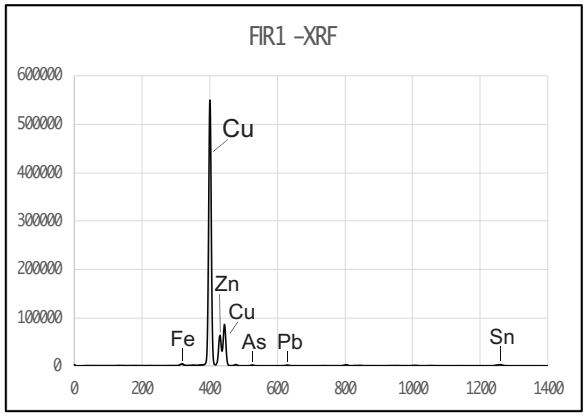
APPENDIX B.13 XRF SPECTRA FROM THE ANALYSIS OF THE SCULPTURE *FIGURA FEMININA*

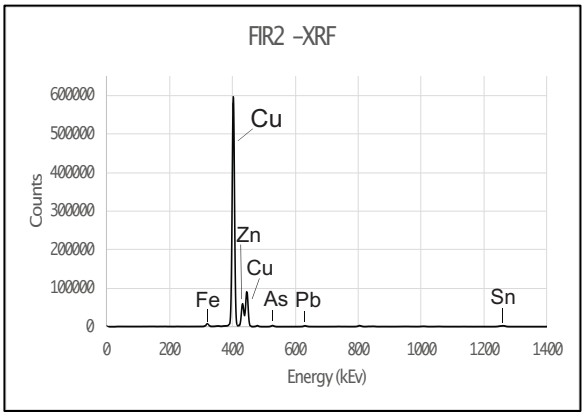


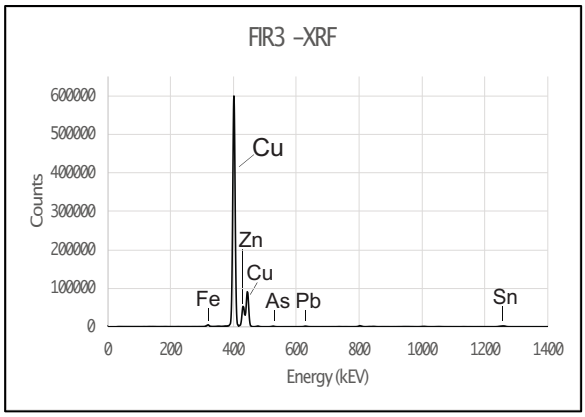
APPENDIX B.14 XRD SPECTRA FROM THE ANALYSIS OF THE SCULPTURE *FIGURA FEMININA*



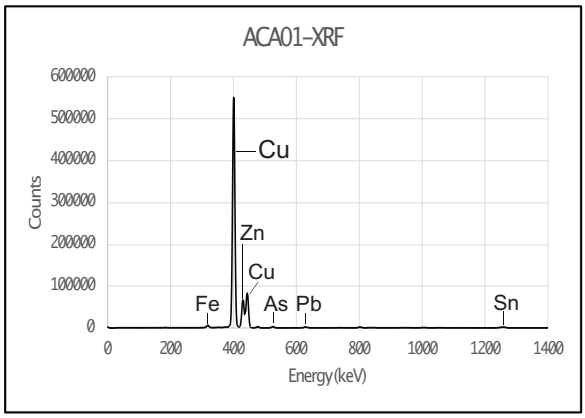
APPENDIX B.15 XRF SPECTRA FROM THE ANALYSIS OF THE *BUST OF FIRMINO*

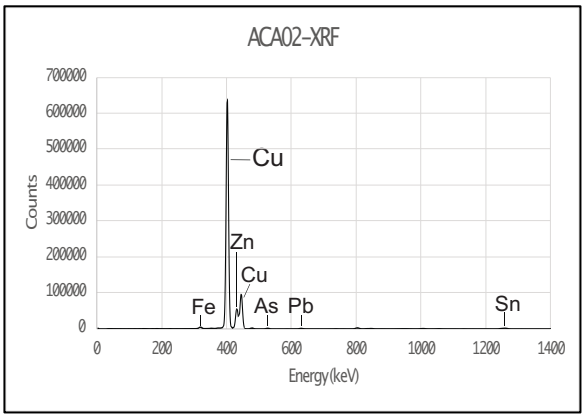


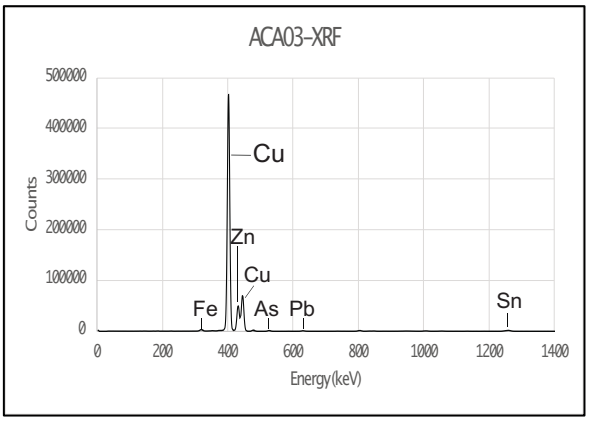




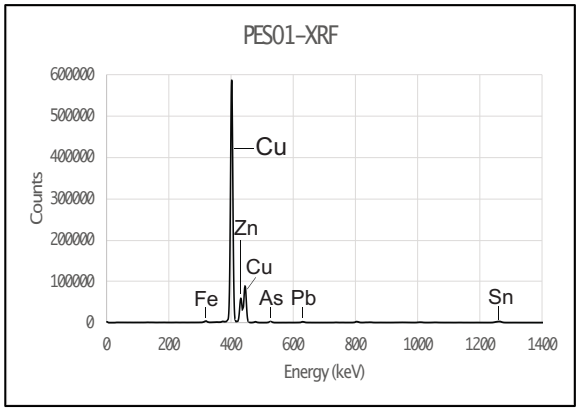
APPENDIX B.16 XRF SPECTRA FROM THE ANALYSIS OF THE SCULPTURE *ACADEMIA - HOMEM SENTADO*

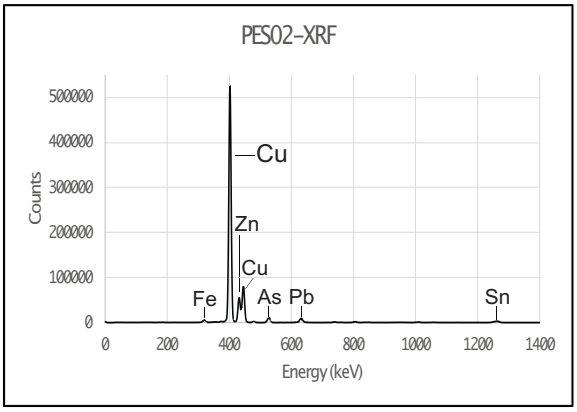


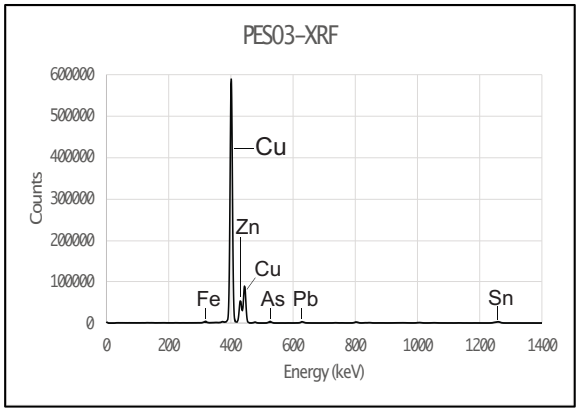


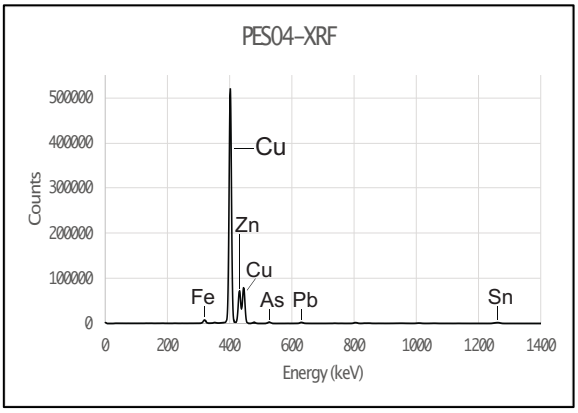


APPENDIX B.17 XRF SPECTRA FROM THE ANALYSIS OF THE SCULPTURE *O PESCADOR*

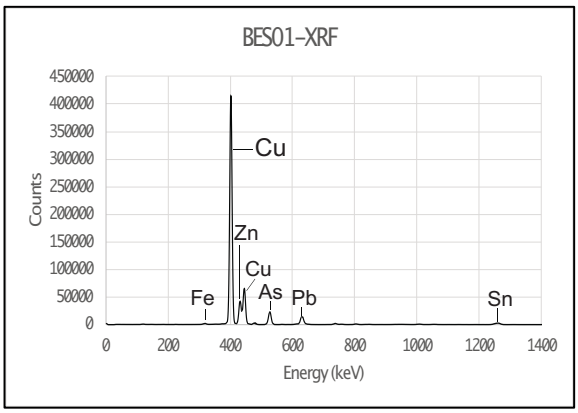


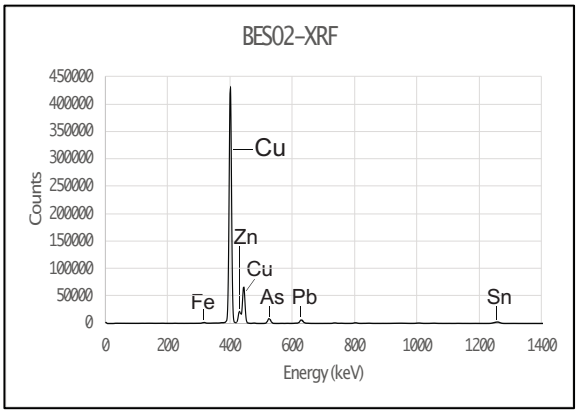


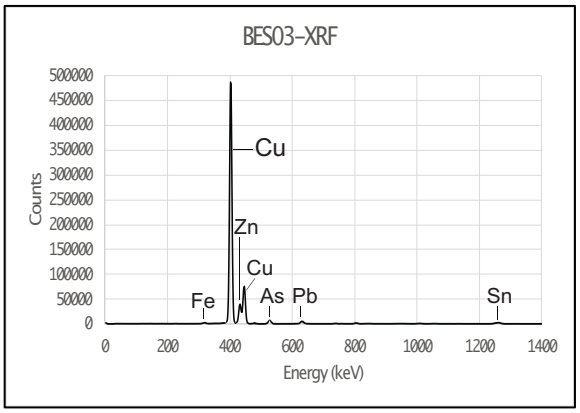




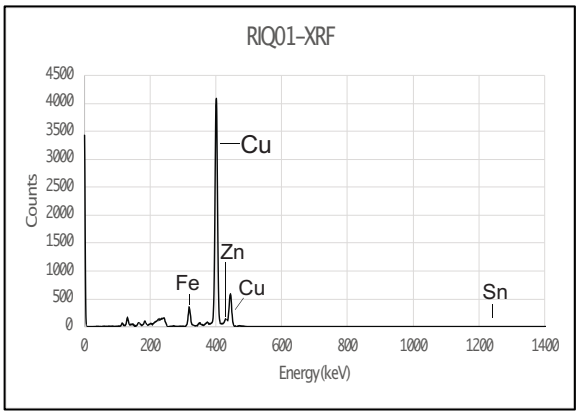
APPENDIX B.18 XRF SPECTRA FROM THE ANALYSIS OF THE *BUST OF FRANCISCO PINTO BESSA*

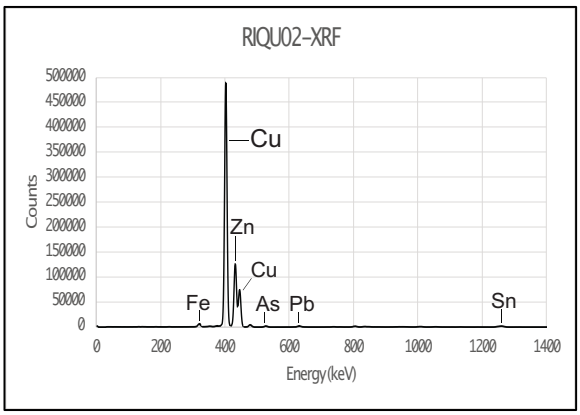




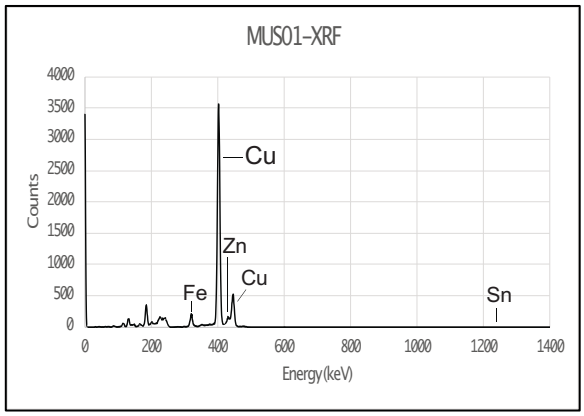


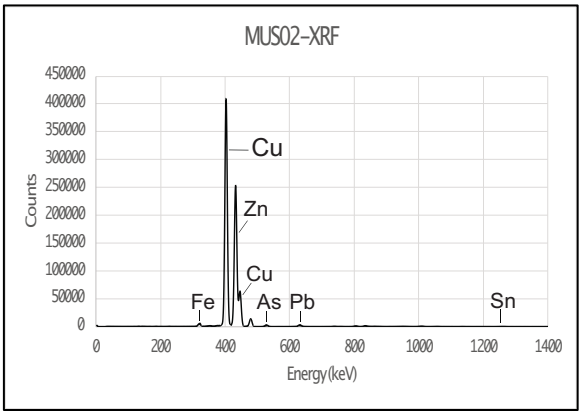
APPENDIX B.19 XRF SPECTRA FROM THE ANALYSIS OF THE *SCULPTURE A RIQUEZA*

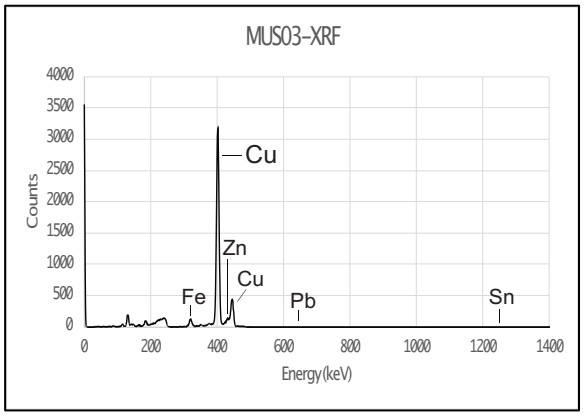




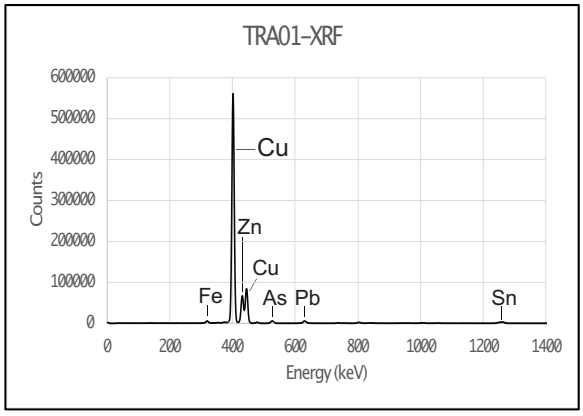
APPENDIX B.20 XRF SPECTRA FROM THE ANALYSIS OF *SCULPTURE A MÚSICA*

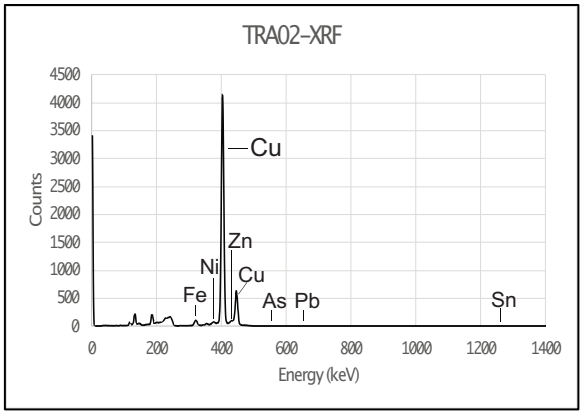


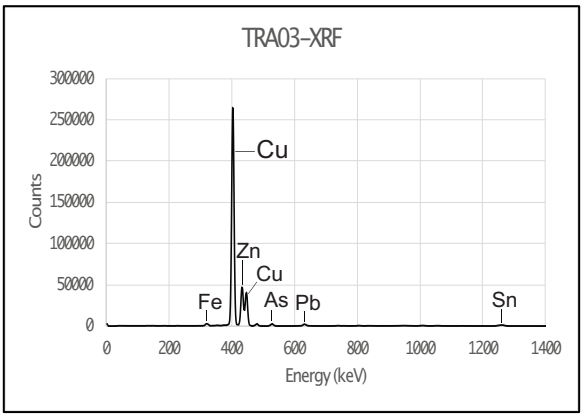




APPENDIX B.21 XRF SPECTRA FROM THE ANALYSIS OF *SCULPTURE O TRABALHO*






TRA03-XRF
300000
250000
200000
150000
100000
50000
0
Counts
Cu
Zn
Cu
Fe
As
Pb
Sn
0
200
400
600
800
1000
1200
1400
Energy (keV)

APPENDIX C SUPPLEMENTARY MATERIAL FOR CHAPTER 7

APPENDIX C.1 QUESTIONNAIRE STRUCTURE AND CONDITIONAL FLOW (SURVEY LOGIC)

This appendix presents the full structure and conditional flow of the survey titled *"Enquiry Flow – Bronze Conservation"*, designed and administered through the Qualtrics platform. The questionnaire included a set of core questions addressed to all respondents, as well as conditional blocks that were activated based on the respondent's institutional affiliation or on their previous answers.

The survey logic was designed to direct specific questions according to two main criteria:

1. The type of institution selected at the start of the questionnaire (e.g. museum, public institution, conservation-restoration company, sculpture foundry, or freelance conservator);
2. The answers provided in earlier sections, which triggered additional blocks when relevant. For instance, if a respondent reported having observed certain types of damage on bronze sculptures, detailed follow-up questions about those alterations or treatments were subsequently displayed.

The structure presented below follows the logical deployment order within the Qualtrics platform, using clear labels to indicate whether questions were:

- Shown to all respondents,
- Shown only to specific types of institution,
- Shown conditionally based on previous answers.

This layout aims to provide transparency regarding the methodological design and branching logic used to collect differentiated data across professional profiles.

ENQUIRY FLOW – BRONZE CONSERVATION

INTRODUCTION

Welcome!

We are glad to invite you to participate in the "methods of conservation of bronze sculptures" survey. However, before deciding whether you want to participate, it is essential to clarify the reasons for this study and what your participation will involve. Please read the following information carefully and do not hesitate to ask us for more details if any questions are unclear or require more information about the study.

Background

Through our research on conservation methods, we have observed that there is a wide variety of approaches to the conservation and restoration of bronze sculptures. These differences are observable in the diversity of techniques and protocols used by professional experts (conservators - metal restorers, art foundry professionals, etc.).

Benefits of this study

No costs or compensation to the participants of this study are foreseen. It is anticipated that the results of this enquiry will provide guidance on the use of available and innovative bronze sculpture conservation tools by all those involved in preserving this type of cultural heritage.

Confidentiality and withdrawal

All information you provide when completing this questionnaire will be anonymous and confidential in accordance with the The European Union General Data Protection Regulation (EU) 2016/679. Participants will not be identified if or when the results are published. Although the questionnaire will ask for your name, institution and e-mail address, these fields are optional. You are free to fill them in voluntarily, as this data is requested for possible contacts in the context of this research.

Who will have access to the information you share?

Only the research team of this PhD project will have access to the information provided by the participant.

Who is responsible for this study?

If you have any questions, don't hesitate to get in touch with Pablo General, principal researcher of this project, by e-mail: pgeneral@ucp.pt

ST. 1 **SOCIO-DEMOGRAPHIC DATA**

Information about you

Name and surname [ ]

ST.1.1

Institution (If you are self-employed, please write "Freelance") [ ]

ST.1.2

E-mail [ ] ST.1.3

Years of experience in conservation - restoration of bronze sculptures

(In numbers) [ ] ST.1.4

Has your institution a metals conservation department?

- o Yes ST.1.5
- o No ST.1.6

How many people work in bronze sculpture conservation in your institution? (In numbers) [ ] ST.1.7

ST.2 **TYPE OF INSTITUTION**

What kind of institution do you work in? Select one of the alternatives.

- o Museum M.1
- o Conservation and restoration company C.1
- o Public institution P.1
- o Sculpture foundry S.1
- o Freelance conservator F.1

Question raised to:
ST.2-M.1 Museums
ST.2-P.1 Public institutions

M.1 **BRONZE SCULPTURE COLLECTION** You may choose more than one alternative.

What kind of bronze pieces are kept in your institution?

- o Busts M.1.1
- o Statuettes M.1.2
- o Human-size statues M.1.3
- o Monumental statues M.1.4

Question raised to:
ST.2-M.1 Museums
ST.2-P.1 Public institutions

M.2 **BRONZE SCULPTURE COLLECTION** You may choose more than one alternative

Where are the above-mentioned pieces located?

- o Busts – indoor M.2.1
- o Busts – outdoor M.2.2

- o Statuettes – indoor M.2.3
- o Statuettes – outdoor M.2.4

- o Human-size statues – indoor M.2.5
- o Human-size statues – outdoor M.2.6

- o Monumental statues – indoor M.2.7
- o Monumental statues – Outdoor M.2.8

Question raised to:
ST.2-C1 C-R Company ST.2-S1 Sculpture foundry
ST.2-F1 Freelance conservators

C.1 **CUSTOMERS**

Who commissions you to restore pieces made in bronze? You may choose more than one alternative.

- o Museums C.1.1
- o City councils C.1.2
- o Foundations C.1.3
- o Individual clients C.1.4
- o Other [ ] C.1.5

ST. 3 **ALTERATIONS OF THE SCULPTURE**

What kind of alterations on bronze pieces have you had to restore most frequently? You may choose more than one alternative.

- o Breakage of the bulk metal (loss of a metal fragment) ST.3-B.1
- o Deformation of the bulk metal (caused by impact or fall) ST.3-B2
- o Other [ ] ST.3-B3
- o Appearance of chloride patina ST.3-PA.1
- o Leaching ST.3-PA.2
- o Roughness patina ST.3-PA.3
- o Other [ ] ST.3-PA.4

ST.4 **PRELIMINARY ANALYSES**

What kind of preliminary processes do you carry out before the conservation-restoration intervention? You may choose more than one alternative

- o Organoleptic (eg. brightness, roughness, etc.) [ ] ST.4.1
- o Microscopy (eg. Optical, SEM-EDS, etc) [ ] ST.4.2
- o Bulk metal analysis (eg. XRF) [ ] ST.4.3
- o Patina analysis (eg. XRD, Raman, etc.) [ ] ST.4.4
- o Other [ ] ST.4.5
- o None ST.4.6

Question raised to:
ST.3-B.1 Breackage ST.3-B.2 Deformation
ST.3-B.3 Other

ST.5 **BULK METAL ALTERATIONS**

If you have worked on a sculpture with a broken or deformed bulk metal, please describe briefly what processes were carried out in the conservation-restoration intervention. [ ] ST.5.1

Please describe the materials you have employed to restore a bulk metal alteration. [ ] ST.5.2

Are reports of these interventions accessible to conservation-restoration professionals?

- o Yes ST.5.3
- o No ST.5.4

In case you answer YES, we will contact you by e-mail.

Question raised to:	
ST.4-PA.1 Chloride	ST.4-PA.2 Leaching
ST.4-PA.3 Roughness	ST.4-PA.4 Other

ST.6 **PATINA ALTERATIONS**

If you have intervened in sculpture with patina alterations, what method of patina removal do you usually perform? You may choose more than one alternative

- o Water under pressure ST.6.1
- o Mechanical or abrasive cleaning ST.6.2
- o Chemical cleaning ST.6.3
- o Laser ablation ST.6.4

Regarding chemical removal, what product have you used (e.g. Rochelle salts, EDTA, etc.)?

[ ] ST.6.5

Are reports of these interventions accessible to conservation-restoration professionals?

- o Yes ST.6.6
- o No ST.6.7

In case you answer YES, we will contact you by e-mail.

ST.7 **PATINA INTERVENTION**

When removing patina, you usually: You may choose more than one alternative

- o Remove the patina until the metallic surface is visible. ST.7.1
- o Remove the patina until the brown patina (cuprite) is visible. ST.7.2
- o Remove the patina leaving some visible green patina. ST.7.3
- o Other [ ] ST.7.4

ST.8 **REPATINATION**

In the restoration, do you apply a new patina to the sculpture?

- Yes (Please explain if you apply hot patina, cold patina, paint, or other product) [ ] ST.8.1
- No (Why?) [ ] ST.8.2

ST.9 **SUSTAINABLE CONSERVATION**

Do you know what sustainable conservation is?

- Yes ST.9.1
- No ST.9.2

Question raised to:
ST.9.1 Yes

ST.10 **SUSTAINABLE CONSERVATION (ST.9.1 YES)**

Are any sustainable conservation measures practised in your institution? If the answer is yes, could you explain which measures are practised?

- Yes ST.10.1
- No ST.10.2

[ ] ST.10.3

ST.11 **PREVENTIVE CONSERVATION**

Do you carry out any preventive intervention to prevent the appearance of natural patina, e.g. microcrystalline wax, benzotriazole or other?

- o Yes Indoors [ ] ST.11.1
- o Yes Outdoors [ ] ST.11.2

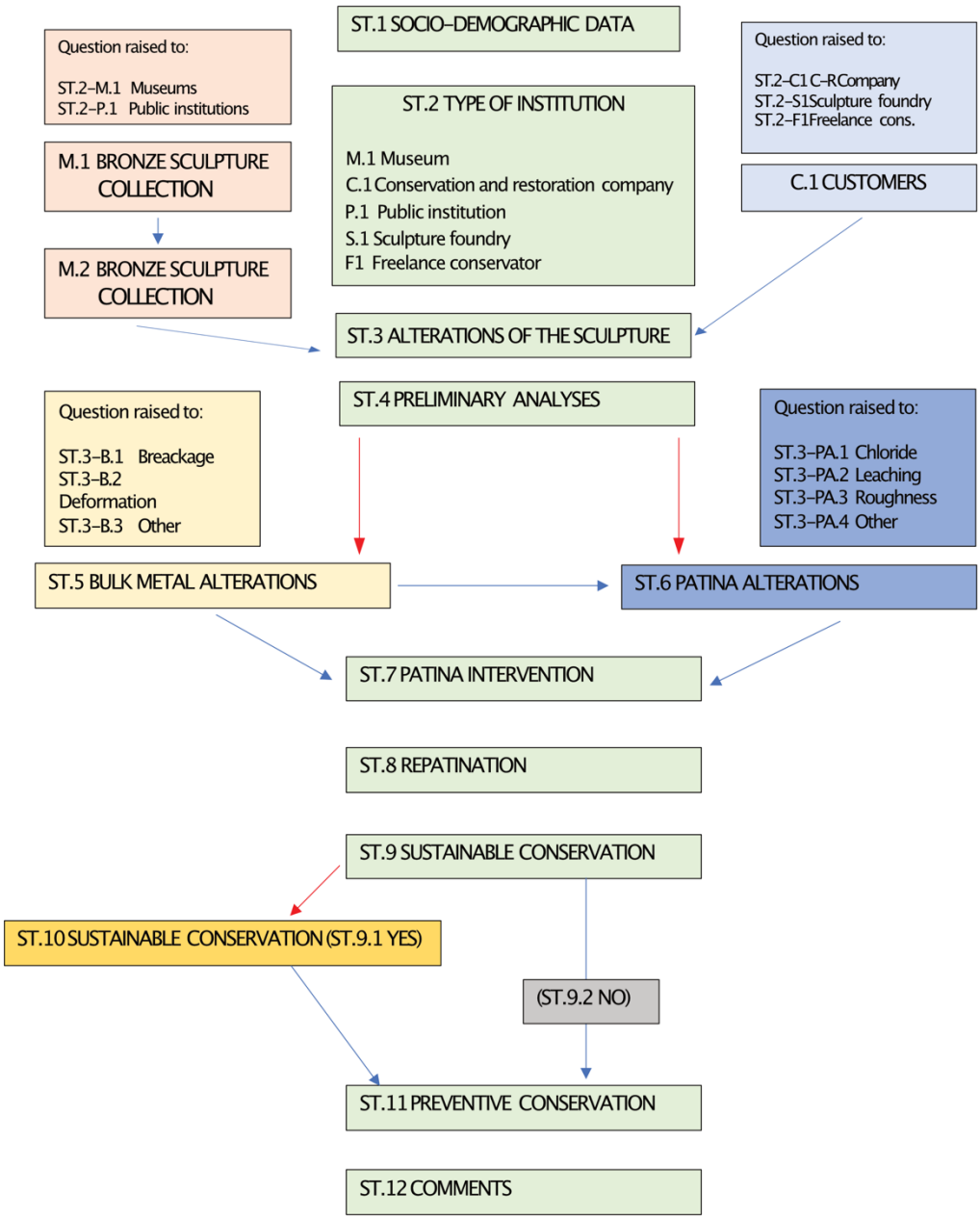
- o No Indoors ST.11.3
- o No Outdoors ST.11.4

In case of preventive maintenance, how often do you carry out interventions (monthly, annually, etc.)? [ ] ST.11.3

ST.12 **COMMENTS**

Should you wish to add anything regarding the procedure of conservation and restoration of metal sculptures, we would appreciate that you do so in this space. [ ]

Figure G.1.1 Survey Logic Diagram – "Enquiry Flow – Bronze Conservation"



APPENDIX C.2. GEOGRAPHIC DISTRIBUTION AND DEGREE OF PARTICIPATION OF RESPONDENTS IN THE BRONZE SCULPTURE CONSERVATION SURVEY

Table C.2.1 - Number of Respondents per Country According to the Percentage of the Survey Completed (100 %, 50–99 %, 10–49 %, 1–9 %)

Country	100%	50 - 99%	10 – 49%	1 – 9%
Portugal	11	2	1	1
USA	9	5	2	3
Spain	9	2	1	–
Netherlands	6	–	–	–
United Kingdom	5	1	–	–
Canada	4	–	–	–
France	4	–	1	1
Chile	3	–	–	–
Argentina	2	–	–	–
Sweden	2	–	–	–
Switzerland	2	–	–	–
Australia	1	2	–	1
Croatia	1	–	1	1
Italy	1	–	–	–
Mexico	1	–	–	–
Greece	1	–	1	1
Denmark	1	–	–	–
Israel	–	–	1	1

APPENDIX D SUPPLEMENTARY MATERIAL FOR CHAPTER 8

APPENDIX D.1 REPORT OF THE WORK CARRIED OUT DURING THE ENDLESS METAL STSM

Report on the outcomes of a Short-Term Scientific Mission

Action number: IG16215

Grantee name: Pablo Andrés General Toro, Research Centre for Science and Technology of the Arts – Catholic University of Portugal

Details of the STSM

Title: **Combining user-friendly electrochemical hardware and a freely accessible application for the chemical analysis of modern copper-based alloys**

Start and end date: 05/06/2023 to 09/06/2023.

Location: Haute Ecole Arc Conservation – Restauration (HE-Arc CR), Neuchâtel, Switzerland

Scientific support: Christian Degrigny (HE-Arc CR).

Technical Support: Haute Ecole Arc Conservation – Restauration: Reference electrode Ag/AgCl (RE), junction tubes and syringes per solution (Evian, KNO_3, NaSesq), stand, clamps, Yoctopuce voltmeter and consumables (polishing paper, Teflon band).

General programme: Implementation of the DiscoveryMat analytical tool to study the chemical composition of copper alloy samples from the casting of 20th and 21st century sculptures from the northern region of Portugal. Training on the operation of the DiscoveryMat hardware and software; data collection; interpretation of results obtained and discussion.

Description of the work carried out during the STSM

Several activities have been conducted, focusing on the application of DiscoveryMat to characterize the chemical composition of copper alloy samples by the monitoring of their corrosion potential (E_{corr}) over time.

A particular characteristic of the samples to be studied is their significant size. Although DiscoveryMat has been proven effective in studying small samples, it has not been previously utilized to examine larger specimens with irregular surfaces, which more closely resemble the characteristics of sculptural pieces. Additionally, it is noteworthy that these samples necessitate a different approach to handling and securing during the measurements compared to smaller pieces.

The first stage of this STSM (Short-Term Scientific Mission) involved assembling the DiscoveryMat analytical tool. It comprises the following components: a Metrohm Ag/AgCl reference electrode (RE) model 6.0733.100 (Fig. 1a) inserted in a Radiometer junction tube filled with one of the solutions used to perform the measurements. A layer of Teflon tape is applied around the glass tube of the RE to ensure that the junction tube is properly secured (Fig.1b).

The Yoctopuce voltmeter (Fig. 1c) is connected to the RE using the white banana plug (Fig. 1d), while a crocodile clamp is attached to the brown banana plug (Fig. 1e). This clamp is then connected to an aluminium

foil underneath the copper alloy sample to analyse, which makes electrical contact with it. The weight of the sample ensures this contact. The DiscoveryMat hardware is controlled by software of the same name (only available for Windows) (Fig. 1f). The Yoctopuce voltmeter is connected to the computer using a USB cable.

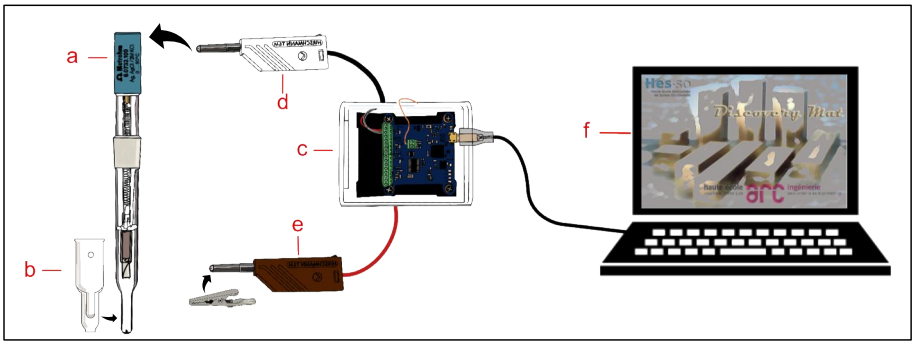


***Fig. 1**. DiscoveryMat instrumentation and setup: a) Ag/AgCl reference electrode, b) junction tube, c) Yoctopuce voltmeter, d) white plug, d) brown plug and crocodile clamp, e) DiscoveryMat software.*

The samples analysed come from four reverberation tubes of sculptures cast in the 1970s, as well as in 2022 and 2023 (Fig. 2). These samples were taken from a foundry in Vila Nova de Gaia, northern Portugal. Due to the irregular surface of the specimens, it was necessary to polish it to improve the results of the analysis (Fig. 3).



***Fig. 2**. Samples studied during the ENDLESS Metal STSM, after cutting them from the reverberation tubes. Samples 1 and 3 correspond to casts from the year 2023, sample 2 is from a sculpture cast in 2022 and sample 4 corresponds to a sculpture cast in the 1970 decade. © Pablo General.*



Fig. 3. *The surfaces of the samples were polished (marked with the red circles) to improve the measurement reproducibility with DiscoveryMat. © Pablo General.*

To achieve the smooth surface appearance for each coupon as depicted in Figure 3, medium-grit SiC papers (240, followed by 360 and 500) were employed to refine the surface, followed by fine-grit SiC papers (1000, followed by 1500) to further diminish roughness, and extra-fine grit SiC paper (4000) for achieving a precise finish. Polishing was carried out under tap water stream to prevent overheating and potential alteration of the metal microstructure.

The four specimens were analysed using X-ray fluorescence (XRF – ThermoFischer Niton XL3t GOLDD with X-ray tube 50kV 2W) to determine the concentrations of elements in the metal alloys (Fig. 4). This information is crucial for integrating the results obtained with DiscoveryMat into the software database.

The DiscoveryMat measurements were carried out using Evian mineral water (pH around 7), a 1% (w/v) solution of KNO_3 in deionized water (pH around 5-6), and a 1% (w/v) solution of NaSesq in deionized water (pH=10). The system RE + junction tube + selected solution must be left to rest for twenty minutes. The RE + junction tube system is then placed in a clamp fixed to a stand and connexions of the voltmeter both to the measuring system and the metal surface to investigate are ensured. An external voltmeter can be used to confirm the electrical contact. The tip of the junction tube coupled to the RE is positioned approximately 3 to 5 mm away from the metal sample (Fig. 5). Figure 6 depicts the DiscoveryMat hardware set up and ready to commence the E_{corr} measurements.



Figs. 4, 5 and 6*. Preparation for the measurement of E_{corr} with DiscoveryMat: fig. 4, analysis of the metals composition to be studied using XRF; fig. 5, placing the RE + junction tube system in the clamp and positioning it over the sample to be measured; fig. 6, DiscoveryMat hardware prepared for the measurement. © Pablo General.*

For the measurement, a drop of solution is introduced using a syringe between the polished surface of the sample and the tip of the junction tube. The operator must then wait a short time (about 3 seconds, necessary to ensure good data communication between the Yoctopuce voltmeter and the DiscoverMat application) before starting the measurement by activating the "scan" button on the DiscoveryMat control panel. The measurements are repeated three times for each solution, two over 5 minutes and one over 15 minutes. A 15-minute scan is deemed successful if the data for the first 5 minutes are between those of the two preliminary 5-minute scans.

Between each measurement, the metal surface needs to be polished with 4000 grit SiC paper under running water, to eliminate any residue from the previous measurement's reactions.

In this study, the results of the measurements of the copper alloy samples in the three solutions showed many differences. The measurements carried out with Evian and KNO_3 were often not reproducible and had to be repeated several times, as shown in Table 1. On the other hand, the measurements with NaSesq went smoothly, with only minor fluctuations, and only three measurements were taken (two over 5 minutes, followed by one over 15 minutes).

Table 1. *Detail of the number of DiscoveryMat measurements performed on the four samples, using the Evian, KNO_3 and NaSesq solutions.*

Sample	Solution	Number of plots
1	Evian	7 (3 = 5 min, 4 = 15 min)
	KNO_3	15 (11 = 5 min, 4 = 15 min)
	NaSesq	3 (2 = 5 min, 1 = 15 min)
2	Evian	8 (7 = 5 min, 1 = 15min)
	KNO_3	4 (3 = 5 min, 1 = 15 min)
	NaSesq	3 (2 = 5 min, 1 = 15 min)
3	Evian	4 (2 = 5 min, 2 = 15 min)
	KNO_3	7 (4 = 5 min, 3 = 15 min)
	NaSesq	3 (2 = 5 min, 1 = 15 min
4	Evian	4 (3 = 5 min, 1 = 15 min)
	KNO_3	5 (2 = 5 min, 3 = 15 min)
	NaSesq	3 (2 = 5 min, 1 = 15 min)

The disparity in the number of measurements conducted with the solutions Evian, KNO_3, and NaSesq is linked to the reaction of these solutions with the copper alloy, producing irregular behaviour in the data acquisition but also the irregularities of the metal surface at the beginning of the polishing process (Fig. 7). Samples 1 and 3 exhibited more irregular measurements when using Evian and KNO_3, in contrast to samples 2 and 4. Conversely, the measurements using NaSesq, when the metal surface was homogeneously polished, demonstrated consistent regularity in all four samples.

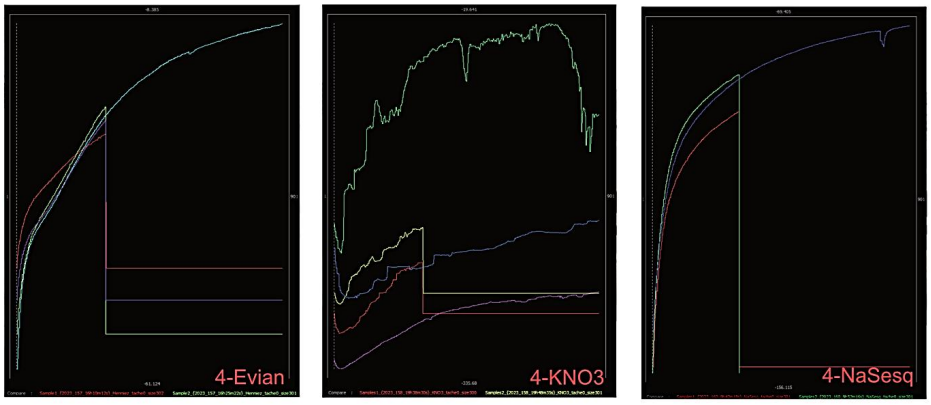


Fig. 7. *Example of distinct plots obtained from sample number 4 using DiscoveryMat in Evian, KNO_3, and NaSesq. Each plot demonstrates the diverse shapes obtained during the measurement process. For KNO_3, only the 15-minute plot in the middle was considered in the data processing. © DiscoveryMat.*

After the measurements, the plots obtained from the four samples, and selected as relevant, were compared using DiscoveryMat algorithm with the entries of DiscoveryMat database. It is important to note that the DiscoveryMat database/library is made up entirely of measurements from previous analyses carried out using DiscoveryMat, following the same protocol as the one described in this report. Over time, the database has been enriched by contributions from various projects. This participatory approach aims to ensure its relevance.

Before this step, additional information is provided to the algorithm about the lack of reproducibility of the plots, the fluctuation of potential values, and the presence of stains on the metal surface at the end of the 15-minute recording, in each solution.

The algorithm then calculates the distance of similarity (dSim) between the plots of the material studied and the plots of the entries in the database, resulting in a ranking of the "proposals". These results are also represented in "graphs", where the plots obtained and those of the entries from the DiscoveryMat library are superimposed by the algorithm.

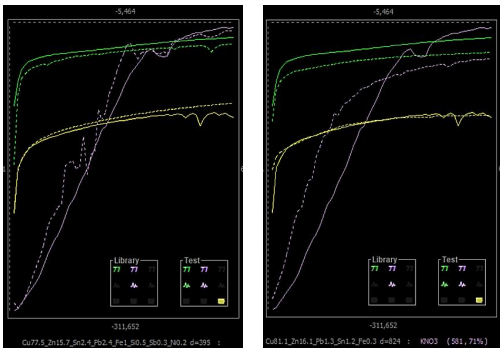
In the "proposals" ranking, attention should be given to the first ten entries that have the lowest distance (dSIM) between the input and the compared entry. They indeed give a preliminary idea of the nature of the material under study. Graphs are then examined, and proposals whose plots intersect at the end of the recording with those of the studied material or follow different slopes are discarded.

By convention we consider that a dSim inferior to 500 corresponds to a good match while if it is between 500 and 1000, it is medium and beyond 1000, it is not a good match. On this basis, the results are as follows:

Sample 1

A good match has been found between the sample plots and those of entries 1 and 3 provided by the database. In entry 1 (Fig. 8), the dSim is 395 and the composition given is Cu 77.5%, Zn 15.7%, Sn 2.4%, Pb 2.4, Fe 1%, Si 05%, Sb 0.3% and Ni 0.2%. Entry 3 (Fig. 9), with a dSim of 824 gives a composition of Cu 81.1%, Zn 16.1%, Pb 1.3%, Sn 1.2% and Fe 0.3%.

As observed in Figures 8 and 9, the parallelism between the plots of sample 1 and those of DiscoveryMat database entries can be seen, particularly at the end of the measurement. The fluctuations of potentials in the KNO_3 plot indicate that the presence of Pb is higher than 1%. The KNO_3 plot is the one that highlights a distinct difference between the two selected entries. While in entry 3, the plot follows a different trajectory compared to sample 1 and intersects with it, in entry 1, the plot follows a similar trajectory to the sample plot, despite the aforementioned fluctuations. Fluctuations in NaSesq of sample 1 at the end of the plot is not understood yet. Fluctuations in Evian water indicated in the inset below the plots seem to be very limited compared to those in KNO_3.



8 9

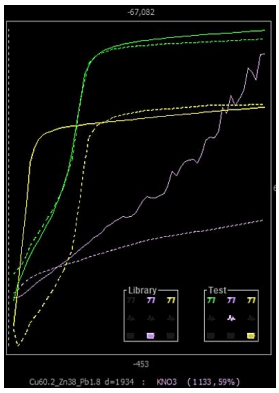
Fig. 8 and 9. *Matching results for sample 1. © DiscoveryMat.*

The composition of the sample according to XRF is Cu 81.7%, Zn 13.9%, Sn 1.9%, Pb 1%, Fe 0.6%, Ni 0.6% and Si 0.3%. When comparing these percentages with the selected entries from the DiscoveryMat database, it can be observed that the closest similarities are found between sample 1 and entry 1, as suggested above.

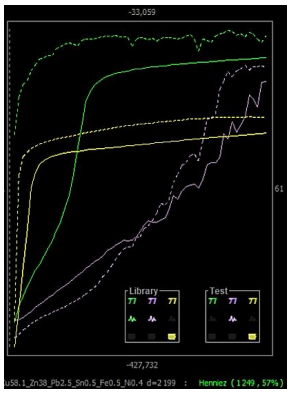
Sample 2

In contrast to sample 1, the matching for sample 2 is not good. Although none of the entries offered by the database provide a satisfactory match for the sample, entry number 3 (dSim 1934 and a composition of Cu 60.2%, Zn 38%, and Pb 1.8%) (Fig. 10) shows a significant match in the Evian plot and coincides at the end of the NaSesq record. However, there is a distinct difference in the KNO_3 measurements, where the entry exhibits fluctuations due to the Pb content exceeding 1% and a different plot profile.

On the contrary, in entry number 7 (Fig. 11) (dSim 2199 and a composition of Cu 58.1%, Zn 38%, Pb 2.5%, Sn 0.5%, Fe 0.5%, and Ni 0.7%), the match is observed for the KNO_3 measurement and runs parallel in the NaSesq plot. However, the match is not as strong for Evian, as the entry plot shows fluctuations that are not present in the sample plot. It is also interesting to observe that the insets characterising the behaviours of sample 2 and entry 7 are similar.



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11

Fig. 10 and 11. *Matching results for sample 2. © DiscoveryMat.*

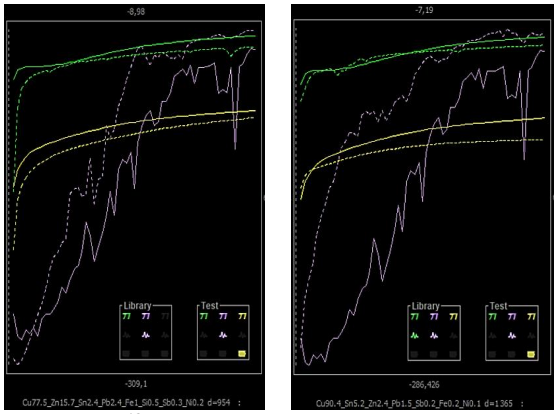
The XRF analysis reveals that the composition of sample 2 consists of Cu 58.7%, Zn 38.8%, Pb 1.5%, Sn 0.4%, Si 0.2%, Ni 0.2%, and Fe 0.2%. These results closely resemble the concentrations of major elements in both entries, but they are more comparable to entry 7 in terms of the types of elements present in the alloy.

The presence of Sn in sample 2, determined by XRF, seems to influence the slope shape in the KNO_3 plot.

Sample 3

Four of the entries given by the DiscoveryMat database have a dSim below 1000, most of them being quaternary alloys. With entry number 2 (Fig. 12) (Cu 77.5%, Zn 15.7%, Sn 2.4%, Pb 2.4% Fe 1%, Si 0.5%, Sb 0.3% and Ni 0.2%, dSim 954), the match is correct in KNO_3 but not in Evian. On the contrary, with entry number 10 (Fig. 13) (Cu 90.4%, Sn 5.2% Zn 2.4%, Pb 1.5%, Sb 0.2%, Fe 0.2% and Ni 0.1%, dSim 1365) the match is with Evian, but not so good with KNO_3.

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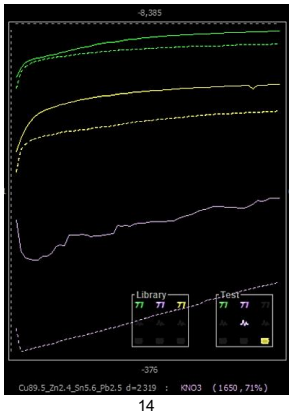
12 13

Fig. 12 and 13. *Matching results for sample 3.© DiscoveryMat.*

This sample, analysed by XRF, shows a composition of Cu 86.2%, Zn 7%, Sn 4.5%, Pb 1.1%, Fe 0.4%, Ni 0.3% and Si 0.4%. Sample 3 is located in between the two entries. However, the matches are not as close as those observed for samples 1 and 2.

Sample 4

In this case, the lowest dSim value is slightly above 1100. Only one match has been found, being entry number 10 (Fig. 14), (dSim 2319; Cu 89.5%, Zn 2.4%, Sn 5.6 and Pb 2.5%). Despite being far apart, the plots are parallel for all three solutions. Only in the case of KNO_3 fluctuations are observed in the analysed metal, but not in the database input. The inserts comparing the characteristics of both sample 4 and entry 10 are rather different. Therefore, we expect a composition of sample 4 different from entry 10.



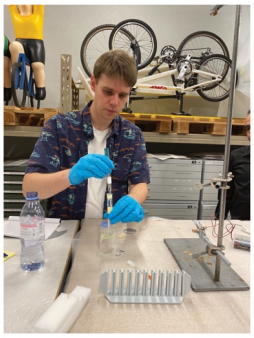
14

Fig. 14. *Matching results of sample 4.© DiscoveryMat.*

The XRF results for sample 4 are: Cu 91.7%, Zn 5.5%, Sn 0.7% Pb 0.7%, Si 0.6%, S 0.5% and Fe 0.3%. As indicated above, if the presence of major elements are recognized by DiscoveryMat, their concentration is not correct.

Other activities carried out in the context of STSM:

- Visit to the Olympic Museum in Lausanne. The STSM participants attended a DiscoveryMat demonstration by Rayan Ammon, HE-Arc CR BA student, on artifacts related to the history of the Olympic Games made of aluminium-based alloys (Fig. 15 and 16).



15



16

Fig. 15 and 16. *Rayan Ammon, BA conservation student at the Olympic Museum. Lausanne, attaching the junction tube to the reference electrode (Fig. 15) and injecting the solution between the tip of the junction tube and the sample to initiate the measurement (Fig. 16). © Pablo General.*

Observing the use of the analytical tool in the context of a museum enabled us to experience the advantages of using DiscoveryMat over any other expensive analyser. However, it is important to understand that DiscoveryMat is a sensitive analytical tool that requires adequate space for operation, which may not be available in many museums. This space is essential for ensuring precise measurements and obtaining reproducible results.

Additionally, the unique physical characteristics of each piece, coupled with their significance in the museum's collection, requires a meticulous examination when selecting the area to be polished and analysed. This careful approach ensures that the visual aspect and readability of the object are not compromised.

- Visit to the Haute Ecole Arc Engineering, at Microcity in La-Chaux-de-Fonds. During this visit, samples of a monumental bronze sculpture, cast in Portugal in 1887, were analysed by optical microscopy and Scanning Electron Microscopy (SEM). With the results of this analysis, which clearly show the stratigraphic layers of metal and patina, as well as a mapping of the elements present in these areas, a MiCorr sheet will be generated. This report will also be included in my PhD thesis, as the analysed sample corresponds to one of the sculptures studied for this purpose.

Description of the STSM main achievements and planned follow-up activities

Although some archaeological bronze samples were initially considered, this STSM focused on modern ones corresponding to sculptures made in the 1970s, in 2022 and 2023 in the Vila Nova de Gaia region of Portugal. The reason for this choice was the physical properties of the latter and possible diversity and proportion of elements present in the samples.

The purpose of the STSM was to acquire proficiency in the use of the DiscoveryMat hardware and software. Some experience is required for the handling of this tool, which is quickly gained through practical application. The software is intuitive and has a guide that makes it easy to use.

The use of larger samples than those usually analysed, of smaller size, allowed the use of DiscoveryMat to be tested on materials with irregular surfaces. It was observed though that it is necessary to polish well the

metal surface to get reproducible results. Although it may seem to be an impediment, this could be done on non-visible or barely visible areas.

The use of three different solutions: Evian, KNO_3 and NaSesq, showed variations in the monitoring of E_{corr}. It was found that NaSesq plots were less irregular compared to the other solutions in the measurements carried out. The lack of reproducibility is partly explained by the fact that the measurements with the first solutions were performed on a recently polished surface, which may have retained some irregularities on the metal and, consequently, generated irregular results in the measured values. In contrast, the NaSesq measurements were carried out on a surface that has been polished many times, reducing the probability of irregularities, and contributing to more consistent results.

The analysis of the four samples using DiscoveryMat allowed us to compare the results obtained with those of the database and gather information about the alloys they are composed of. Furthermore, their XRF analysis make them as new entries in the DiscoveryMat database. Expanding this library will enable other users to find more precise matches when analysing their metal objects with DiscoveryMat.

This STSM has been a great opportunity to get to know and experience first-hand a low-cost electrochemical instrument that can be very useful for the chemical determination of metallic materials.

In addition, the opportunity to work in parallel with two other colleagues in STSM was very beneficial. It also provided me with an on-site insight into the assembly system and operation of Pleco, as well as the process of accurately creating a MiCorr sheet.

The experience gained in using DiscoveryMat will make it easier to disseminate this knowledge to the academic community and to conservator-restorers. This STSM should also be the first in a series of scientific collaborations between HE-Arc CR and the Research Centre for Science and Technology of the Arts - CITAR - UCP in the field of conservation-restoration and the application of low-cost, portable and easy-to-use devices like DiscoveryMat and other devices such as Pleco and MiCorr, which HE-Arc CR is currently developing.