Historical Copper- and Lead Alloys at the Plantin-Moretus Museum, Antwerp

Alloy compositions, corrosion phenomena and conservation recommendations

Proefschrift voorgelegd tot het behalen van de graad van doctor in
de conservatie-restauratie aan de Universiteit Antwerpen te verdedigen door

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Promotoren
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Faculteit Ontwerpwetenschappen
Departement Erfgoed – Opleiding conservatie-restauratie
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Notes to the reader

Lines in *Italic* are quotes from literature sources

Words marked with an asterisk * can be found in the Glossary

The abbreviation [Arch.] is used to relate to archival documents in the Museum Plantin-Moretus

The Glossary and abbreviations list are in the Attachments

All photographs were taken by the author unless otherwise indicated

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The image on the cover page is a type metal microstructure of an 80-12-8 % Lead-Antimony-Tin alloy at 5000 x magnification with a Scanning Electron Microscope.

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Historische koper- en loodlegeringen in het museum Plantin-Moretus, Antwerpen

Legeringsamenstellingen, corrosie fenomenen en conservatie aanbevelingen

Proefschrift voorgelegd tot het behalen van de graad van Doctor in de conservatie-restauratie aan de Universiteit Antwerpen te verdedigen door Patrick Storme

Promotoren:
Prof. dr. Joost Caen
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Antwerpen, 2018

Foreword

Standing on the sidelines, looking in on my life, I am amazed at how things have turned out. There seems to have been a succession of coincidences that have led me from one situation to the next. I've always tried to view the world with a sense of beauty. A wide range of interests has taken me to places and introduced me to exciting people whose existence I could never have even imagined. I was destined to become an architect until I realised I preferred the applied fine arts. There was never any need to make choices because there was always something or someone suggesting I do this or that. There was for example a fellow student who, from out of nowhere, told me to go and study jewellery design. Even though I'd never heard of this option, I nonetheless went with it and began a course at the Royal Academy for Fine Arts in Antwerp. When I graduated, my former professor, Wim ibens, asked me to come and work with him on completing the reconstruction of the shrine of St. Gertrude in Nivelles. This beautiful 13th century shrine, which was an exceptionally progressive design and became the template for all the major gothic cathedrals in France, was bombed in the Second World War leaving only a number of deformed remains. The creation of this replica in silver with gilded parts, precious gems and enamel turned into a six-year adventure, during which I learned many aspects of the art of jewellery making and silversmithing. The ground was laid for a love of old and antique objects.

With this basic training in gold and silversmithing, my work in the area of metal restoration began. In the early stages of this journey, conservation increasingly caught my attention as a more subtle discipline within the subject. My job as assistant at the National Higher Institute for Fine Arts in Antwerp resulted in a partnership with a number of colleagues and the setting up of the Conservation-Restoration unit in 1988. This education course has since undergone numerous changes, and was eventually integrated into the University of Antwerp. Research had meantime become very important within the world of conservation, and because we always endeavoured to keep up with international standards, the conservation-restoration education evolved into a unique course in Flanders (Caen, 2009).

In the broader field of conservation application and research topics, there was one specific request from the Museum Plantin-Moretus that attracted my attention. The staff there had discovered corrosion on some of the lead type letters. Given that this collection is recognised around the world for its incredible historical significance, research was needed to establish the cause of this corrosion and to find solutions for the museum. From this moment on, my personal interest in Plantin-Moretus as a museum, its history, the knowledge and innumerable historical objects grew even stronger.

While I have never held much sway with the idea of destiny, I do believe that coincidences together with certain initiatives, observations and support from those around me have always been of the utmost importance. The road that has led me to this point would not have been so easy to travel without the support of numerous colleagues from the conservation-restoration course. Decades of teamwork have created a sort of family bond for which I am especially grateful.

The evolution from conservation-restoration to conservation research has also resulted in a more intense collaboration with the Department of Chemistry. It would not have been possible to start this PhD without the efforts of my two supervisors, Prof. Dr. Joost Caen and Prof. Dr. Karolien De Wael. They have supported me on this journey, each from their own specialism, each with dedication and patience. No less important was the contact with the Museum Plantin-Moretus and its collection, but to an even greater extent the contact with the people working there such as the director Mrs. Iris

Kockelbergh, Mr. Pierre Meulepas and Mr. Guy Hutsebaut. With regard to the specific research on the copper matrices, I received stimulating input from the emeritus director Dr. Hendrik Vervliet and Dr. Goran Proot, to whom I am immensely grateful.

During the course of the research, I met many people from many different disciplines, all of them inspirational and helpful. I would hereby like to express my heartfelt gratitude to Dr. Olivier Schalm for the joint reflections on the chemical aspects, Dr. Paolo Piccardo and Dr. Carla Martini for the use and interpretation of the results from micro-hardness testing, SEM-EDX and Raman, Dr. Lorenzo Rolla for conducting ICP-OES measurements on my samples, Jean-Pierre Smet for macro hardness measurements, Dr. Erik Fransen for the statistical work on the XRF results, Dr. Bart Vekemans for his assistance with the IMMACO standards, Dr. Gert Nuyts for SEM-EDX and Raman measurements, Dr. Koen Janssens, Dr. Frederik Vanmeer and Dr. Ermanno A. Clerici for conducting micro-XRD testing on lead corrosion products. It would have been impossible for me to bring this work to such as successful conclusion without their efforts.

Unfortunately, it is not possible to list everyone I have met in my life, even though they have all played a role in the choices I have made, in enriching my knowledge and experience, in making me the person I am today, and in helping me navigate the roads that I have travelled. Last, but by no means least, I would like to thank my dear wife Kristin, our children Sofie and Steven, family and friends. They have been extremely patient during the various emotional stages of this journey. To each and every one of you, my sincerest thanks.

PAUSE STRANGER: YOU STAND IN A

COMPOSING ROOM

HERE METAL STAMPS CALLED TYPES
ARE ASSEMBLED BY SKILFUL HANDS
INTO THE MASTER-PATTERNS
FROM WHICH THE VISIBLE WORD IS MULTIPLIED

FIVE CENTURIES AGO
THE INVENTION OF MOVABLE TYPE
OPENED A NEW EPOCH IN HUMAN HISTORY
BY RELEASING THE COMMON PEOPLE
FROM THE THRALLDOM OF ILLITERACY
AND SETTING THEIR FEET UPON THE ROAD
TO SELF-GOVERNMENT

YOU WHO TRAVEL THAT HIGH ROAD
TOUCH NOT WITHOUT REVERENCE
THESE LEADEN SYMBOLS OF YOUR FREEDOM
REMEMBER YOUR INCALCULABLE DEBT
TO THE COMPOSITOR
WHOSE PATIENT, NIMBLE FINGERS BUILT FOR YOU
LETTER UPON LETTER

A THOUSAND STAIRWAYS TO THE STARS

Inscription written for the Monotype Corporation, by the great typographer Beatrix Warde, to display the capitals of their new typeface ‘Poliphilus’.[1]

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[1] Piccolo Press Ltd.: Wedding Stationery - Information & Price List, Nairn, 2011.

Introduction

Appendix

This part comprises all executed XRF measuring results on the matrices from the Plantin-Moretus collection, including notes and comments presented in a separate volume.

1 General introduction

With my background in gold- and silversmithing as a designer, practitioner and conservator-restorer, the focus in this thesis is on the material- and technical aspects of the metal items used in hand press printing, more specifically from the Plantinian collection which dates back to the 16th century.

The Plantin-Moretus Museum is world famous not only for its unique collection of books, prints and archives, but also for its handpresses and tools for the printing process, such as punches, matrices and the lead printing letters, all situated in the original family house. It was the first museum to be included on the UNESCO world heritage list.[2]

The conservation of the museum and its content is a challenging task because of the vast number of items and the wide variety of materials, all kept within the historic house in the centre of Antwerp. Conservation directives are therefore not straightforward and the situation demands close monitoring and scientific research to optimise the conditions for safely storing and exhibiting the objects.

Fig. I: Museum Plantin-Moretus exterior view on the left, the printing presses and type cases on the right.

2 Conservation objectives

Cultural heritage covers a range of aspects, from landscapes, sites and buildings to objects, music, and traditions, etc. The conservation of metal objects is the main topic addressed in this work. Conservation research serves the common goal of preserving a maximum of information from the past and keeping the material evidence in an optimal condition for future generations. The latter involves studying the conditions of the materials and their deterioration in the environment in which they are kept.

Objects can be conserved by taking preventive measures such as optimising the climatic conditions in the museum or the showcases. In many cases, however, conservation also means taking action with regard to a certain object to keep it in good condition or to restore it to a desired condition. Over the centuries, conservation techniques have developed from the artisanal repair of deteriorated or damaged objects to a research-based discipline where conservators apply specific treatments to retain, enhance and maintain the desired aspect of an object. Preserving information that is present

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[2] Website UNESCO: http://whc.unesco.org/en/list/1185, consulted 19.12.2017.

on the object or in its materials may also be a goal, and in some cases (e.g. archaeological objects) the historic information even becomes more important than the object’s presentation.

Ethics and ethical problems in metal conservation are generally similar to those in other fields of cultural heritage conservation. Nonetheless, several specific problems arise only in metal conservation practice, causing a loss of the original information. Examples include the heating of archaeological objects for corrosion removal, radical conservation-restoration interventions on technical objects to make them work again, the continuous cleaning actions and severe wearing of silverware, etc. Taking action as a conservator at the current point of the object’s lifespan often requires a well-balanced opinion that takes all known or researched facts into account. The history of the object as well as its expected future comes into view and determines the nature of the treatment that may be proposed.

Preventive conservation is a critical issue in the preservation of metallic objects. The main objective is to prevent corrosion in all its aspects and a clean, stable and foremost dry climate is therefore ideal. In reality however, it is usually impossible to control the environmental conditions in such a way that metals will not corrode at all. Moreover, metals in objects are often combined with organic materials such as ivory or wooden handles on tea- or coffeepots, which require higher humidity levels for their preservation. In many cases, these factors restrict the possibility of maintaining ideal parameters for the metals.

3 Conservation research

The usual goal of research in conservation is to detect and implement better techniques, products and environmental conditions to enhance the preservation of objects. The presence and integrity of objects, preferably in their context, act as witnesses of the historical, cultural or technological identity of mankind. In the case of the Plantin-Moretus museum and collection, they represent a very important phase of human development from the 16th to 19th century in Western Europe. Keeping the collection in the museum in the best possible condition is therefore an extremely important task where conservation and research meet. It also facilitates research on typography and its related items such as printed books, illustrations, maps, archives, etc. Researchers that focus on the historical material evidence study the corresponding shapes of the steel punches and the copper matrices struck from them. Additionally, the lead printing letters (called ‘types’) could be used to retrieve information if no punches or matrices survived. In the past, the lead type was considered of lesser interest due to the supremacy of the punches and matrices, which without a doubt hold the most accurate keys to historic typography. The majority of studies were based on visual features of the typefaces, punches or matrices. The punches are the primary information source for attributing faces (letter models) to certain punchcutters, but many punches are missing. This leaves us with the surviving matrices, which are the closest counterparts to the punches. As a conclusion, it is interesting and useful to concentrate the present conservation research on the metals in the museum’s collection.

Metal conservation

Among cultural heritage objects, metals cover a wide field of applications. Metals are well known as the constituent constructive elements for important large scale objects such as buildings, bridges, statues, machines, etc. On smaller scale many objects are made from metal or from alloys, spanning weaponry, armour, household items, tools, jewellery, silverware, clocks, bells, coins, etc.

Metal conservation comprises all acts that lead to a better preservation and disclosure of metallic artefacts. Applied research is an important factor of the metal conservation trajectory and may serve different goals. The two main fields for metals are a) studying the corrosion layer or the corrosion behaviour and b) analytical research on the microstructure or chemical composition.

Degradation processes on metals primarily start on the surface, resulting in corrosion formation. The development of the corrosion process incorporates a loss of original material which may lead to a complete loss of object until mineralization. Three main environments are commonly considered: atmospheric conditions (outside, inside; most important relative humidity and air pollution), soil conditions (soil composition, depth, humidity, pH and amount of gasses) or marine conditions (soluble salts, water depth, amount of dissolved gasses, direction of water currents and the role of both microscopic and macroscopic living organisms). In the light of this study, the atmospheric conditions of the Museum Plantin-Moretus are of primary importance. These conditions, combined with the composition and microstructure of the metals that must be preserved, determine the corrosion processes and their evolution.

Research on the Plantin-Moretus collection

In the 1960s, attention was for the first time focussed on preserving the Plantin collection by the conservator at the time, Dr. H.D.L. Vervliet. Dr. R. Sneyers of the Royal Institute for Cultural Heritage (KIK-IRPA) provided instructions for the safe-keeping of the many woodcut printing blocks in the collection.[3]

In 2008, new conservation research was initiated by the University of Leuven (KUL) and KIK-IRPA to monitor air quality and lighting conditions in the museum. This resulted in a report (Van Bos en Watteeuw 2009), followed by an extended version in 2010 and a third phase report in 2012 (Van Bos en Watteeuw 2012). Adjacent to this research project, a survey was set up to investigate damage to books, documents and showcases. The results of this project were presented in 2012 (Peckstadt en Moris 2012). That year, the Chemistry Department of the University of Antwerp (UAntwerpen) set up scientific equipment to measure air particles and volatile gasses. These results were presented as separate reports (Krupińska, De Wael, & Van Grieken, 2012) (Krupińska, Van Grieken, & De Wael, 2013).

Research was conducted in 2012-2013 because of a corrosion problem on a number of the preserved lead types, resulting in a publication on the topic (Storme, Jacobs, & Lieten, 2013).

Analytical measurements were seldom used on typographical materials, except when a conservation problem arose. Examples are iron-gall inks that ‘burn’ through the parchment or paper, lead type that is corroding or the acidification process of more recent paper sheets.

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[3] Oral information from dr. H.D.L. Vervliet, 2017.

4 Objectives of the thesis

This conservation-orientated study tries to unite different fields of research. Historical-archaeological research, typographical research, historic material-technical research and conservation research are considered complementary, leading to possible new insights. In this respect, the objective of the thesis is to introduce analytical techniques to improve knowledge about the collection of the Museum Plantin-Moretus (MPM). Two groups of items within the collection are targeted: the collection of lead type and the copper matrices.

Type is commonly known to consist of lead, with additions of tin and antimony. Former research (Storme, Jacobs and Lieten 2013) has revealed that some compositions in the museum collection are more susceptible to corrosion. From this premise, it was considered important to investigate the relationship between composition and corrosion development. First, analytical measurements are performed on the lead type to differentiate the strongly corroding items from the less corroding ones. Secondly, corrosion experiments are executed to mimic corrosive atmospheres. Evaluation methods are used to link the types' compositions to the corrosion development. Outcomes from the research should result in directives to enhance conservation planning to safeguard the future of this important collection. Additionally, the analytical measurements are used to get a wide view on the oldest lead types in the museum's collection.

The collection of copper matrices in the museum is already studied in depth on typographical grounds, in some cases complemented with observations on their visual appearance. Based on the characters that they bear, a number of matrices together with the steel punches are attributed to a certain punchcutter. In some cases, the matrices are in conjunction with archival documents in the MPM. However, it is not always certain that the attribution of certain matrices was performed accurately since anybody who acquired the punches was able to produce the matrices himself. However, this attribution can be viewed in two ways. To the typographical researchers, it is important to identify the typeface and relate it to a certain punchcutter. In this sense, the majority of punches and complementary matrices have been attributed with a high certainty and reliability. However, a number of strikes and matrices are not attributed to anyone, often because the typeface could not be retrieved from prints or matched with a certain designer or punchcutter. Finding a correlation in copper alloy composition between known or well-documented matrices could deliver some insight into the kind of copper that was used by a certain matrix-maker, as well as the period or the location. Combining these findings may help unravel the origin of a number of non-attributed sets of strikes or matrices.

The final objective of the thesis is two-pronged: on the one hand to find correlations between material features and historical facts for the lead types and for the copper matrices; on the other, to draw conclusions from the physical-chemical research on the lead type alloys and transfer the results into useful conservation directives. This information can be used by the museum's staff to enable improved preventive or mitigation actions for securing the future of this valuable collection.

5 Structure of the thesis

The first chapter briefly covers the MPM and its collection. Historical sources on the knowledge about hand press printing processes, including lead type compositions, the casting of lead type and the production of copper matrices are listed and critiqued.

Chapter 2 comprises known historical and contemporary physical-chemical information, more specifically on the lead and copper and their alloys with a link to the objects studied in the museum collection.

Chapter 3 summarises the specifications of the analytical techniques and instruments used in the following chapters.

Chapter 4 presents the production of experimental cast lead alloys with historical compositions as used to make printing types. These alloys are used as references to calibrate the X-Ray Fluorescence (XRF) instrument that is used for measuring historical types from the Plantin-Moretus collection. The reference alloys were investigated on their composition by ICP-OES, on macro- and micro hardness values, with optical and scanning electron microscopy for their element distributions and phases. Subsequent XRF-analyses on historical types from the MPM were executed.

Chapter 5 takes a look at the analytical measurements on the copper matrices to detect the possibilities of using XRF as an in-situ analytical technique. The respective compositions of the matrices are expressed in elemental ratio graphs in order to show possible correlations. The numeric results were also used with multivariate analysis techniques to form clusters. The outcomes from these measurements are expected to deliver data complementary to earlier historic research on the matrices sets, their designers and producers, localisations and time period.

Chapter 6 focusses on the corrosion of type, more specifically the differences in lead type alloys and the influence of the most frequent added metals, i.e. tin and antimony, on corrosion development. A number of analytical techniques are used to define corrosion products and their development: gravimetric and colorimetric measurements, optical and scanning electron microscopy, electrolytic measurements, Raman and X-Ray Diffraction. This chapter also includes the conservation directives for the lead types in the MPM collection.

Chapter 7 includes the conclusions.

The attachments provide additional information, as indicated throughout the thesis.

An appendix is attached, which includes all the XRF data and comments on a large selection of strikes and matrices from the museum's collection.

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1 The museum Plantin-Moretus and historical-technical research

Content

LABOR et CONSTANTIA[1]

1.1 The Plantin-Moretus museum

1.1.1 The Plantin and Moretus generations[2,3]

Christophe Plantin was born in France, probably in 1520, perhaps earlier. He became a journeyman bookbinder and arrived in Antwerp together with his wife Jeanne Rivière and his daughter Margareta in 1548 or 1549. The 'Officina Plantiniana' was established in 1555 but it was not until 1576 that he settled down at the 'Gulden Passer' (Golden Compass) located at the Vrijdagmarkt, where the museum is still situated today. As the first 'industrial' printer, he proved to be a genius autodidact and a prominent figure in the history of book-printing, after Johannes Gutenberg. His exceptional legacy, with publications on humanism and sciences, is regarded as of utmost importance for Western civilisation. He established a print shop (1583), not only in Antwerp but also in Leiden, as a possible escape route when political or religious situations took a turn for the worse. A Parisian division (1567) of the Officina was run by one of his sons-in-law, Gillis Beys.

When Plantin died in 1589, the print shop was taken over by Jan Moretus I (1543-1610), his son-in-law from the marriage of his second daughter, Martina (1550-1616). From then on, the Moretus generations managed the business through the heydays of the 16th and 17th century until the difficult times in the 18th century leading to the closure of the print shop in 1870.

Jan Moretus I was already an apprentice with Plantin at the age of 14. He worked and studied hard, and eventually became the 'shop keeper' at the Officina. This meant that not only was he responsible for selling the books but he also played a central role in developing business relationships and in all the administration. The printing and bookshop were located in 'de Grote Valk' on Kammenstraat in Antwerp until 1576. In that year, the printing activities were moved to the Vrijdagmarkt and the bookshop remained in the Kammenstraat. On Plantin's death, Jan Moretus I inherited everything in the print shop, i.e. the houses, all the typographical material and all the books that were in stock. He

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[1] Printer's device of the Plantin print shop

[2] (Voet, 1969-1972), p. 3-256.

[3] (Voet, 1996), p. 9-32.

was in charge of the Officina from 1589 until his death in 1610. He worked and lived in ‘de Grote Valk’ until the death of Jeanne Rivière in 1596, who lived until that time at the Vrijdagmarkt. In that year, Jan Moretus I moved to the ‘Gulden Passer’. It is worth noting that he was able to establish the reputation and high standards of the Officina Plantiniana partly with the cooperation of his good friend Peter Paul Rubens, who designed book illustrations.

Another important person in the Officina was Frans Raphelengius (1539-1597), who also became one of Plantin’s sons-in-law by marrying his oldest daughter Margareta (1547-1594). He worked as a well-educated proofreader and corrector at the Officina. With the death of Plantin and the allocation of almost everything to Jan Moretus I and only a small part to the other children, Jan Moretus I took the lead in the conservation and re-direction of Plantin’s belongings, keeping in mind that the Officina as a business had to be guaranteed for the future. The solution was a more or less equal distribution between each of the five heirs. Raphelengius received the Leiden shop and was allowed to run a bookshop near the Cathedral in Antwerp, as a filial of the bookshop of the Officina, on Kammenstraat.

The second generation of the Moretus family were Balthasar I (1574-1641) and Jan II (1576-1618). Balthasar was well educated, having attended the Augustines in Antwerp and private studies with Justus Lipsius in Leuven. He was paralysed in his right arm and learned to write left-handed. It is thought that he suffered from low esteem and he never married. Little is known about Jan II but it is assumed that Balthasar worked at the print shop and Jan II lived and worked in the bookshop until his death. This was however a very difficult time for Balthasar, having lost his strong brother. He found a new companion in Jan van Meurs, who worked at the bookshop until quarrels led to the end of the business relationship in 1629. From 1632, his nephew Balthasar II helped him to run the Officina.

Balthasar II represents the third generation, managing the print- and bookshop from 1641 until 1674. It was in this period that the houses and courtyard that we can admire today were completed. Being a true master-printer and businessman, he was socially engaged and set up a health insurance system for his workers. He married Anna Goos (1627-1691) and had twelve children, eight of whom survived. His first-born son, Balthasar III, represents the fourth generation.

Balthasar III (1646-1696) acted as a mirror to his father by becoming very socially active in Antwerp, but also showing off his wealth and well-being. Nonetheless, being a true business man, he faced a severe crisis because of the political and economic decline of Spain in the 17th century. Since most of his orders were placed by the Hieronymite monks, this led to a decrease in orders and payments. His visit to Madrid to settle the difficulties resulted in a monopoly for the ‘rezo romano’, meaning that the Antwerp print shop was ensured for all future orders of liturgical books to Spain. He was married to Anna Maria de Neuf (1654-1714) and had six daughters and three sons. One of the sons was Balthasar IV (1679-1730).

The fifth generation is composed of three individuals, namely the widow Anna Maria de Neuf, who worked in the Officina from 1696 until her death in 1714. Balthasar IV joined the Officina in 1707 and together with his brother, Joannes Jacobus, became joint owner of the Officina in 1714. With the death of Balthasar IV in 1730, everything passed down to Joannes Jacobus. From his marriage with Theresia Schilder (1696-1729), the eldest son Franciscus Joannes followed his father into the printing business. In the meantime, the family had invested in real estate, stocks and shares and other means, becoming less and less dependent on the printing activities to maintain their high standard of living.

In 1750 Franciscus Joannes Moretus (1717-1768) married Maria Theresia Josepha Borrekens (1728-1797). The printing business was a kind of side-kick for Franciscus, but in a period of diminishing graphic design practitioners, he made great efforts to find the best illustrators of the time to produce elaborate books. In 1764, however, disaster struck as all foreign privileges were revoked. The 'rezo romano' came to an end and the solid foundation of the company disappeared. Nonetheless, the quality of the books had become well known internationally and a number of customers were still loyal to the Antwerp print shop. However, production levels were still well below those in the past.

After the death of Maria Borrekens in 1797, the Officina was equally divided between their five remaining children. Political instability forced the family to scatter around Europe and it was not until 1808 that the Officina was officially represented by Frans Jozef Moretus until his death in 1814. From that year on Lodewijk Frans Moretus tried to establish a new business plan, after the Napoleon decree had led to the strict regulation and control of foreign printers. However, this was not very successful and his heir and cousin Albert Moretus (1795-1865) closed the printing business in 1840. A last attempt was made by Edward Moretus to restart, but this failed finally in 1870. The Moretus family handed over the housing and all of its content to the city of Antwerp in 1876. It was an act of great significance, enabling the city of Antwerp to preserve this magnificent cultural treasure.

1.1.2 The museum

Today, the museum still houses magnificent sixteenth- and seventeenth-century renaissance rooms and courtyard as memorabilia from past centuries of luxury and wealth. However, of primary interest for the history of typography are the 'Officina', the casting room, the letter room, the print shop, the correctors' room, the bookshop and the office of the printer-publisher. Elaborate historical information about the buildings, interiors and library of the Plantin dynasty has been described in detail by Voet (Voet, 1969-1972). Together with these magnificent historical settings, there are the typographic collections with printing presses[4], the punches, matrices, type, drawings, woodblocks, copper plates and adjacent materials and tools. The copper matrices and the lead type are the predominant objects of interest in the present study.

The collection of types is internationally renowned. Some of the rarest standing types are exhibited: texts in Latin, Greek, Hebrew, Chaldean and even Ethiopian faces. As stated by the type specimens ('letterproeven'), we know that Plantin had over 90 different typefaces. He also managed to build large material inventories so that his successors only had to provide new fonts. Plantin bought his material from the best Flemish and French specialists of the time with a level of respect to integrated quality that was unprecedented. He always looked for the best to print certain works, independent of what was available in Antwerp. The print shop therefore houses a large number of punches and matrices, created by the most important letter-cutters and designers of the sixteenth century. The museum has today approx. 4,500 punches, 20,500 matrices, and 62 typefounders' moulds, together representing 90 letter series such as Roman, Italic, Gothic, Civilité, but also music, Hebrew, Greek and Syrian. Many revivals of these fonts are still found in the typography of today. The lead type collection holds an estimated few millions of pieces.

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[4] More on printing presses in: '*The decline of the common press*', Gaskell, P.: Cambridge University Ph.D. thesis 2902 (1956) and '*A New Introduction to Bibliography*', Gaskell, P.: Oak Knoll Press (1972), p. 118-124.

The historic housing house with its many rooms, floors, basements and recently renewed interiors offers a large variety of atmospheric conditions in which the objects are kept. Showcases and a climate system were introduced to maintain temperature and humidity levels within the desired museum conditions. However, the historic house includes an abundance of oak windows with glass panels that are not insulated, as well as oak floors, beams and furniture. These factors may cause conservation problems, which are addressed in Chapter 6.

1.1.3 The collection

The Plantin-Moretus Museum is a true memorial to the great Netherlands 'Archi-typographus', housing a unique assembly of all aspects related to handpress printing and the trade that went along with it. The famous library with its exquisite prints and books, but perhaps more importantly the Plantinian archives, are completed with the presses, the lead types, copper matrices and the extremely valuable cut steel punches from the most famous typographers of their times, such as Garamond, Granjon, Le Bé, Van den Keere and others.

We are first and foremost indebted to Plantin and his successors, the Moretus generations and related to them the Raphelengius family, for having preserved the materials and archives as best they could, even in difficult political or economic times.

Around 1850, the printing house became obsolete and business slowed to a complete stop under Edward Moretus. Already well aware of the importance of its comprehensive collection, the 'Gulden Passer' house with all of its content was acquired by the city of Antwerp in 1876, which installed a museum and opened it to the public in the year 1877. After being hit by a V-2 bomb in 1944, the museum was re-opened in 1951 and stayed more or less unchanged until 2016 when a new makeover gave the museum a new flair from September 30 onwards. In the meantime, UNESCO World Heritage acknowledged the importance of the museum and its collection, rewarding it in 2002 with a nomination and effectively listing it in 2005 as the first museum ever to be regarded world heritage.

The focus for the present study is on lead types and copper strikes/matrices from this collection. The number of lead type pieces is unknown but could be estimated at three to four million.[5] The exact number of copper strikes/matrices is somewhat difficult to pinpoint from the existing lists, because in some listings (e.g. the Adlib electronic database, to be consulted online), strikes are not always counted as matrices. The website gives a total of 20,062. The Parker-Melis Inventory of 1960 lists 4,485 strikes and 16,011 matrices, giving a total of 20,496. Within the scope of this study, all boxes with strikes and matrices were photographed (see a separate folder in Attachments) and all strikes and matrices in each box were counted, giving a total of 20,498, as of December 2016.[6] The full list is available in the Attachments.

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[5] Estimated calculation on the average number of type sets in the MPM, by Mr. P. Meulepas, administrative assistant.

[6] Note: MA 82 b-e were not available at the time of photographing and counting, hence the number mentioned by Parker-Melis, 193, is included in the total.

1.2 History of printing[7,8]

The history of printing goes back to the birth of homo erectus, when illustrations acted as an individual expression or a source of information. For a very long time, works of art that represented a scene or symbols that could be understood by others were in fact unique objects. When the need for transmission or storage of information became imminent, duplication techniques were developed. Clay tablets, rolls and books of parchment with hand copied texts were among the first sources of information to be spread more widely; but even then, the information was only accessible to a relatively limited group of people. Besides the fact that one had to be able to read the characters or the symbolic meanings within illustrations, the art objects and books remained very expensive, valuable and vulnerable.

The first application of printing is to be found in China, when the government needed to spread information over a huge area to a large number of people. Around 1041-1048, Pi Sheng would have used movable type (individual characters) for the reproduction of documents. He made negative impressions with a set of type, composed to a text, in a kind of fine clay. After baking this impression, it served as the printing plate with mirrored characters, inked and pressed on to damp paper, leaving the image readable. This laid the foundations for reproductive printing. In the 14th century, Wang Chen ordered approx. 60,000 characters to be cut in wood for the purpose of printing the Chinese history of technology. He would also have invented a rotating compartmented cases system to hold this vast number of characters for easier distribution to the text composer. In the same period of time, in 1403, King Taejong in Korea ordered the first set of 100,000 types to be cast in bronze. This technology was used until the 16th century.

In the Middle Ages in Europe, handwriting and illumination of documents were highly admired forms of art although the main purpose was to retain and distribute information. The use of iron gall or sepia inks on parchment, beautifully decorated with costly paints and gold leaf, reached its peak in the 14th and early 15th century. Such books became more exquisite and expensive while economic, social and ideological developments in this period were crying out for a new means of communication.

Besides the printing system itself, the expensive and laborious process for making parchment also had to be replaced by a medium that was cheaper and easy to mass-produce. The transmission of paper to Europe under Arab domination penetrated from Spain (9th century) and Italy (12th century) into France (13th century). Papermaking became more common in the 13th century whilst France and Germany set up their paper-making centres in the course of the 14th century. It remains unclear why the concept of movable type would not have been imported at the same time. In any case, right at the dawn of the printing era around 1450, paper had been thoroughly experimented with and was available from widespread, continuous available and qualitative sources.

Xylography, or printing from woodcarvings, developed as well in the Far East as it did in Europe. Together with the use of paper instead of parchment, it was found to be very suitable for making illustrative prints and short pieces of text. Wood engravers became more skilful and in the first half of the 15th century small books with several pages appeared. In contrast to wood carvers, who cut the

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[7] (Lechêne, 2015)

[8] (Pittion, 2013)

image along the grain of the wood, the engravers used crosscut wood, which allowed for much more detailed work as well as being much more able to withstand the printing process. Illustrations and text was often combined and, much later, when metal printing was introduced, the woodblocks remained the optimal medium for relief printing besides copper engravings that were introduced for intaglio printing.

In contrast to the Far East alphabets, which consisted of many 10s of 1000s of character blocks, the Middle-East and Western alphabets only had a few dozen characters, supplemented with accents, numbers and punctuation marks. It was therefore a logical but more importantly a feasible step towards transferring the existing uses of metal dies and punches from the gold- and silversmiths into movable metal type for printing. This invention, largely attributed to Gutenberg, was developed in the mid-15th century. Until now, it remains debatable exactly which experiments and technological developments had taken place in this period, before the metal movable type was designed into an operational system for printing as we know it. The only witnesses from that time are the prints and books. Many attempts and studies have been carried out in this area with the major restriction that only this second-hand information is available. There are no known remnants either of the earliest printing dies or type, or the instruments that must have accompanied them. Only texts or illustrations that are scarce or that remain open for interpretation are available', such as the illustration by Jost Amman, 1468. (Fig. 1.1 and Fig. 1.2) Even this source of information is already relatively late, as printing would have been invented around 1450.

The metallographic printing system in its developed form consists of a die that bears the impression of a letter of the alphabet. This die is made by first cutting a steel punch with the mirrored character at the end. With this punch struck mostly in a small rod of copper, the die (called a matrix), is fabricated. This matrix in its turn was placed in an ingot mould or 'instrument'. This mould holds the space for the body of the letter. When put together, a lead or tin alloy is poured into the instrument, producing a printing letter or type cast as a result. This was repeated as many times as the printer needed numerous type pieces to compose the pages for the book he was planning to print. Simultaneously, the invention of the printing press was needed to allow a high production throughput of printed pages in large quantities. This is also attributed to Johan Gutenberg in 1450. The most convincing evidence for this is from Gutenberg's associate Johann Fust, whose grandchild Peter Schoeffer wrote in 1505 in a preface to an edition of Livy that 'the admirable art of typography was invented by the ingenious Johan Gutenberg at Mainz in 1450'. It remains a point of discussion whether this is proof or merely an account that allows Schoeffer to claim the invention for his family.

The system of punches, matrices and cast lead type was maintained into the 20th century, although improvements with automated machines were introduced in the late 19th century with the monotype and linotype production machines. For some specific applications, stereotypy was used frequently in Paris in 1790 and consisted of impressing a full page in clay or soft metal with characters, on which a complete print plate in a lead alloy was cast to use as the print die. Stereography in 1797 used a composition of a full page of copper mirrored and positive matrices, on which a lead alloy was cast to function as the printing die. From 1830 on, galvanic applications were used to copy die plates by means of electrotyping. After WW II, photosetting and digitisation began to set in.

Fig. 1.1: Jost Amman 1568, a typefounder at work, casting a tin or lead alloy into a mould to make series of printing letters, collected in the basket on the floor.

Fig. 1.2: Jost Amman 1568, a printing shop with compositors in the background, while co-workers are inking and changing paper at the press.

Modern processes now define ‘printing’ more broadly than ever before. Reproducing texts and illustrations is no longer limited to fixed materials as carriers. Information media and audio-visual means have changed our way of reading and viewing. Television, computer and smartphones offer almost unlimited access to all kinds of information, as well documents, photos and moving images. Further developments involve the integration of information in our daily life and surroundings, as is already demonstrated with glasses and built-in projectors, environment-enhanced city and museum guides on tablets, virtual reality headsets and so on. The speed with which technology and applications is changing, could also lead to a loss of durable information. If this happens, art and books may well become the sole witnesses of our history.

1.3 Historical research

1.3.1 Research on typography

Gutenberg is considered the European inventor of printing with movable type, although rivals have claimed the invention. The Gutenberg question has always been a matter of research and debate over the centuries. Discussions on this matter exploded around 1900 when scholars such as Schoeffer, Hessels, Zedler and Schwenke played important roles in this matter (Dane, 2011). From a printer's point of view, Charles Enschedé's typefounding experiments were an important source of information, in many aspects different from the more theoretical researchers (Enschedé, 1901). Later into the 20th century, incunabula were studied by Lotte Hellinga, Hendrik Vervliet, James Mosley, Paul Needham, Joseph Dane and many others. Still, valid questions about the way Gutenberg actually cast his type remain. In recent years fresh attention has been focused on the subject by Paul Needham and Blaise Agüera y Arcas, because Gutenberg's printed letters vary so considerably. Their observations suggest the use of techniques other than punches and matrices for producing the printing type. The fact is that we have no documentation or proof for the first decades of Gutenberg's work. The year 1450 is considered the year that printing with movable type was introduced, but there is no evidence before the 1470s for the use of steel punches and matrices as a system for producing type. There is an account of a visit by Nicolas Jenson to Mainz in October 1458, where he was sent by Charles VII of France to discover more about the 'people skilled in cutting punches'. Gutenberg's first steps towards the development of movable type is however still unknown. Since he was a metalworker, producing large numbers of pilgrim badges and mirrors, he was acquainted with the techniques for doing this on a large and economically prosperous scale. He also must have known of the technique used by goldsmiths to make coins and letter-punches. Combining these techniques in order to produce pages of text is most probably to be put on his account. However, the exact process of evolving from separate punches to a mirrored page of text to be printed on paper could easily have taken many years and many different trials before succeeding. Many of the suggestions made earlier may all contain a grain of truth and none of them should be ignored. It is only logical that the most versatile and economical technique developed from all the others. Further reading on this topic can be found in Tanselle's bibliography (Tanselle, 2002) and James Mosley's personal bibliography (Mosley, 2010).

At the Plantin-Moretus museum, a first inventory of the printing types was made up by Max Rooses and published in 1905, 'Index characterum architypographiae Plantinianae'. Later studies were executed by Leon Voet, Harry Carter, Parker and Melis, Hendrik Vervliet and others.

Until now, archival and historical research was performed mainly from the mid-20th century on while discovering and cataloguing the Plantin-Moretus collection. There has never been a wide-scale attempt to use chemical analytical measurements on the collection because there was no reason to do so, while at the same time, there were no analytical instruments that could be used at the museum site. However, some analyses were made by Harry Carter while he was studying the Antwerp collection.

Carter, who was curator at the time of the Oxford University Press, acknowledged the importance of the Plantin collection and presented his first work on the matter in 1955: 'Specimen types from matrices at the Plantin-Moretus museum'. This was followed in 1956 by a publication in De Gulden

Passer 34: ‘Plantin’s types and their makers’. The first study which included the printing material itself rather than the printed matter, appeared in the ‘Inventaris van de stempels en matrijzen van het Museum Plantin-Moretus’ (Parker & Melis, 1960). Very shortly afterwards, an updated and revised version of this work was presented (Parker, Melis, & Vervliet, 1960).

Later studies concentrated primarily on the origins and evolution of typefaces or on the social-economic activities of the families Plantin and Moretus. Examples for this are to be found in the works ‘Sixteenth-century printing types of the Low Countries (Vervliet, 1968) and ‘The golden compasses: a history and evaluation of the printing and publishing activities of the Officina Plantiniana at Antwerp’ (Voet, 1969-1972). The last quarter of the 20th century provided little new data or insights on the Plantin collection, until it was picked up again by Dr. Vervliet and led to a number of new publications on the typefaces origins and their significance in printing (Vervliet, 2008) (Vervliet, 2010). It seems that there is new interest in the collection and the historical facts of the development of typefaces, mostly from a typographer’s point of view. Meetings and courses given by the Plantin Institute are successful with scholars from the history department of the University of Antwerp and students from graphics and design courses.[9]

With the development of photographical and electronic techniques, printing began to change drastically in the 1960s. Conservators of historical collections with typographical material going back 500 years, started to fear for the loss of significant facts and knowledge. The most important collections began to be explored and examined for future generations: the Oxford Printing Office, Paris (Imprimerie Nationale), Lyon (Typographic museum), Sweden (Stockholm), Haarlem (Enschedé), Parma (Bodoni), Treviso (Tipoteca) and Antwerp. Nowadays, there are still an important number of researchers working on typographical collections, such as John Lane, Paul Nash, James Mosley, Stan Nelson, Fred Smeijers, and Nelly Gable (the latter three are actual punchcutters in the old tradition).

1.3.2 Typeface designers, punchcutters, matrix makers and justifiers

Typefounding as practised in Europe and the West consists of three stages in its fully developed system form: punchcutting, the making of matrices and the actual casting of the printing letters in hand moulds, holding the specific matrix (Moxon, 1683).

The production of a typeface as a printed letter starts with a design and the cutting of a set of steel punches. The punchcutter had the most important influence on the design of the printing types of his time. Although the modern concept of the ‘type designer’ did not exist in the early days of printing, the punchcutter was the designer and executing craftsman (Knight, 2012). It is unclear to what extent 15th or 16th century punchcutters used drawings to construct their characters or if they used alternative methods such as modelmaking or impressing the punch they were carving from time to time in a soft material (clay, lead), to check the forms and dimensions. It is known that some (e.g. Jaugeon, Fra Luca Paciola) used precise drawings to define the compositions of their characters. These were mathematical models from early handwritten scripts.

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[9] Initiatives and courses by the Plantin Institute of Typography can be found at: http://www.plantininstituut.be/

In the transition period towards prints with movable type, the character of the script was maintained by three features: the angle of the edge of the pen to the writing line, the weight of the letters (width by height) and the shape or structural form of the letters, commonly expressed clearly in the n and the o (Fig. 1.3 and Fig. 1.4). As for the construction of the letters, the pen strokes were defined as the number, the order and the direction of each of the strokes to build each letter (Knight, 2003 & 2009).

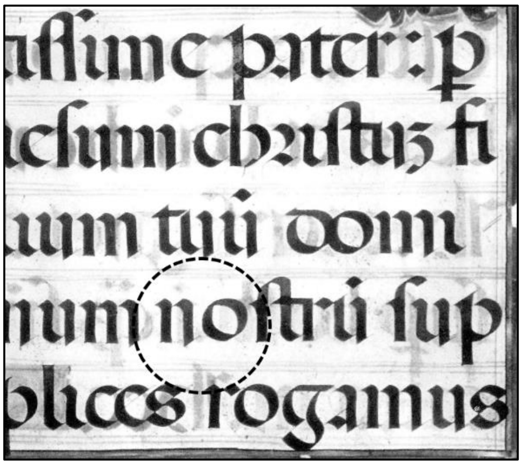

Fig. 1.3: Carvajal Missal, Rome.[10]

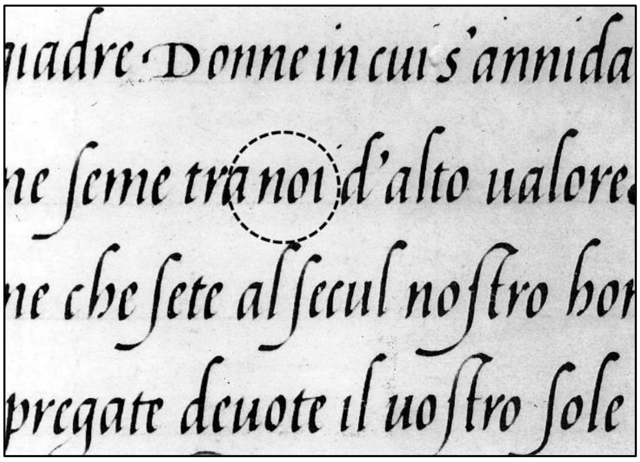

Fig. 1.4: Handwritten Specimen Book, Siena 1545 by Bernardiono Cataneo.[11]

An early and important figure in the early days of printing and type design is Jenson, working in about 1470 in Venice. He appears to have taken some fine examples of humanistic script as a basic model for his Roman type (Fig. 1.5). It is quite obvious that he must have been making arbitrary decisions for the final definition of the letters he was about to cut into punches. Unlike for the Venetian Roman types, it was considered easier to engrave blackletter or gothic types because they had to faithfully follow the original calligraphic models. It still is credited to Gutenberg and/or Schoeffer that the characters and the setting of the textura gothic in the 42-line Bible is of the greatest achievements (Knight, 2012), (Fig. 1.6).

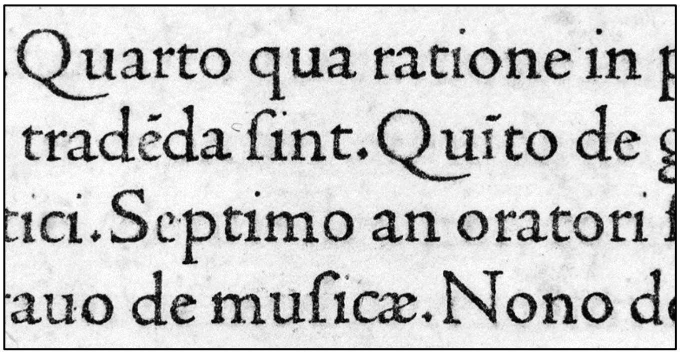

Fig. 1.5: Jenson Roman type print.[12]

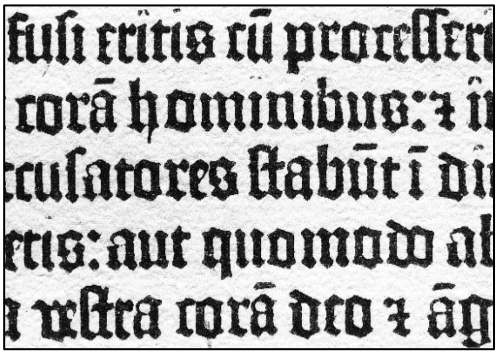

Fig. 1.6: Gutenberg's 42-line Bible.[13]

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[10] (Knight, Historical Scripts from Classical Times to the Renaissance, 2003 & 2009), p. 85

[11] (Knight, Historical Scripts from Classical Times to the Renaissance, 2003 & 2009), p. 97

[12] (Olocco, 2017)

[13] (Knight, 2012), p. 17

Regardless of the way in which a punchcutter defined the characters that he wanted to cut, either from examples, from drawings, straight from his head or by repeatedly printing in a soft material to refine the design while cutting, the skill of the old engravers of type is regarded as greater than all others involved in the book production process. These punches are the first step and the most valuable goods that a punchcutter possesses. From these punches, 'strikes' are produced which are the rough imprints of the punch, usually into the surface of a copper rod. This was usually done either by the punchcutter himself, or by the person who bought the punches, allowing him to produce new strikes whenever he liked. The justification* of strikes to obtain fitting matrices for the 'instrument' that the type caster wanted to use to produce a lead fount (a complete set of lead printing letters, 'type', to start printing), was mostly done by the type caster.

The most important type cutters in the framework of the present study of matrices in the Plantin-Moretus collection are described below.

1.3.2.1 Claude Garamond

Born c. 1510 he became perhaps the most important punchcutter of all time. He was an apprentice in the years 1525-1534 and a journeyman until 1538. His life is well documented from 1540 onwards. In the subsequent ten years, he cut his Romans, early Italics, Royal Greeks and his first Hebrews. His 'seconde taille' Romans and later Italics were cut between 1548 and 1561, the year he died (Vervliet, French Renaissance Printing Types, 2010). The work of Garamond is widespread, because he devoted his life to punchcutting and selling matrices across Europe. From 1555 onwards he also supplied Plantin with matrices for all sizes of his Romans, except for the smallest, which he never cut (Carter, 1960). In 1563 Plantin also bought another 10 sets at the executor's sale in Paris, after Garamond's death.

1.3.2.2 Robert Granjon

Robert Granjon was born in Paris around 1513 as the son of the bookseller Jean Granjon. He was a bookseller and a punchcutter, travelling frequently to Lyons and, after having married and lived there, leaving in the mid-1560s for Antwerp to work for Plantin and Silvius (Vervliet H. , 2017). In the early 1570s, Granjon stayed in Frankfurt, Paris and Lyons, which he left in 1577 for Rome, where he died in 1590. Granjon was a talented man, had innovative ideas and was very productive. He developed and cut nearly ninety typefaces: 30 Italics, seven civilités, nine Greeks, 20 Romans, two or three Hebrews, a dozen exotics, half a dozen music typefaces, and an unknown number of initials, arabesque ornaments and fleurons. His average production came close to two typefaces per year. Besides the selling of books and cutting punches, it is important in this context to note his trade of selling matrices throughout Europe. Printing types from his matrices were available in France, Italy, Spain, the Netherlands, and the German-speaking and Scandinavian countries until the end of the 18th century (Vervliet, 2010). Along with Van den Keere, mainly for type and in some cases punches and matrices, Granjon was Plantin's main purveyor of punches and matrices from the end of the 1560s to the 1580s. The MPM has preserved 25 sets of punches or matrices attributable to Granjon.

1.3.2.3 Guillaume Le Bé I

Born in Troyes c. 1523-1524 he became an apprentice with Robert Estienne in Paris in 1539-1540. In 1545 he left for Venice to cut Hebrew faces and produce matrices and moulds for Giustiniani and others. In 1550 he returned to Paris (Carter, 1960). He cut 19 faces between 1545 and 1591. His Hebrew in particular are highly respected in typography circles for their beauty and historical influence. The MPM collection holds at least 5 sets of matrices that are definitely his (Parker & Melis, 1960). When Garamond died in 1561, Le Bé bought most of his punches and matrices and started a large collection of work by the best French masters. He traded in strikes and matrices and sold a number to Plantin and in Frankfurt. He died in 1598.

1.3.2.4 Hendrik van den Keere, the younger

Van den Keere was probably born in 1540-1542 in Ghent. His grandfather had bought the typefoundry belonging to Joos Lambrecht in 1553 when the latter left the country, and his father Hendrik van den Keere the elder was an important printer in Ghent (Vervliet, 1968). Hendrik van den Keere the younger was often referred to as Henri du Tour, the French form of his name. He began working for Plantin in 1568, and from 1570 on, he was the only purveyor of type to Plantin. He is known for his series of 10 Flemish blackletters the punches from which have survived and are kept at the MPM. More importantly perhaps are his seven Romans, which were cut in the 1570s. Van den Keere cut punches in three successive body styles: the first until 1569-1570, the second from 1570 to 1574 and finally the third from 1574 until his death in 1580. About 40 sets of matrices in the MPM are attributed to Van den Keere (Parker & Melis, 1960). In addition to his punches and matrices, it is worth noting that a great deal of documents such as bills, correspondence, account books and posthumous inventories in the minutest detail have also been preserved. These documents give us a very good picture of how a typefoundry operated at that time. After his death, his material was sold to Plantin and his foreman caster, Thomas de Vechter. The latter took the material with him to Leiden (Vervliet, 1968).

1.3.2.5 Francois Guyot

Being a Frenchman of origin, Guyot worked in Antwerp between 1539 and his death in 1570, except for 1568 when he stayed in London. His arrival in Antwerp filled a vacancy in the typefounding trade left when De Keyser died in 1536 (Vervliet, 1968). During the last 20 years of his life, he was a very important punchcutter and letterfounder. He cut Romans and Italics in a particular style compared to the Parisian faces, but they were considered very usable with a strong character and their popularity lasted well into the 18th century across Europe. There are four sets in the MPM collection (Parker & Melis, 1960). An early Italic (fat-faced 2-line Double Pica 280 mm) set of matrices is preserved at Nordiska museet, Stockholm (NS 21) and in the MPM (MA 174) (Vervliet, 1968). The attribution of this face to Guyot in the 1540s is solely based on style.

1.3.2.6 Ameet Tavernier

Tavernier was born in Belle (now Bailleul, French Flanders) in about 1522. As an Antwerp contemporary of Guyot, he was taught by Joos Lambrecht just like Hendrik van den Keere. It is known that he cut Romans and blackletter. His types appear from about 1550. A face, based on the Flemish writing of the 16th century, was the first of its kind and was called Civilité (MA 163). It is considered possible that he might have created more of the early faces in the MPM. The international role of Antwerp at the time meant that Tavernier's types were used across Europe. Tavernier also sold sets of matrices in Flanders, the Netherlands and Frankfurt. He is rated less highly as a punchcutter than Granjon, Garamont and Van den Keere, nevertheless his types were used by many printers over a long period of time. This in itself proves that the quality of his work was respected. He was co-opted by Plantin, who granted him the certificate of proficiency. Sadly enough, Tavernier died soon afterwards in 1570 (Vervliet, 1968).

1.3.2.7 Pierre Haultin

Haultin was born c. 1510 and worked mostly in Paris (1562, 1565-1567) and La Rochelle (1571-1587), except when prosecution threatened, at which point he moved temporarily to Geneva (1550) and Lyon (1550, 1563) (Vervliet, 2010). He was a punchcutter and type caster and supplied printers? all over Europe (Vervliet, 2008). Roman, Italic and Greek types by his hand were used as early as 1557 (Carter, A view of Early Typefounding up to around 1600, 1960). Eleven faces are listed in the Parker-Melis Inventory, marking him out as a crafted punchcutter. He is known for his quest to find the economic use of types, hence the narrow proportions and large x-heights of his Romans, called the Dutch style. A set of his Nonpareil Roman and italic survive at Oxford (Parker & Melis, 1960). His nephew, Jérome, settled as a type-caster in London in about 1568. Pierre Haultin probably died in 1587 or 1588 (Vervliet, 2008).

1.3.2.8 Jacques Sabon

Originally from Lyon where he was born in 1535, Sabon worked from 1555 in Frankfurt and then spent some years wandering around before returning to Frankfurt in 1564 (Meldau, 1935). In the spring of 1565 he moved to Antwerp to work for Plantin, mostly as a typefounder. He was however also a punchcutter, known for his large capitals. While in Antwerp, he completed Garamond's 'Grosses capitals Extraordinaires (MA 78 and MA 9). Later he returned to Frankfurt to marry Egenolff's granddaughter, after which he took over the typefoundry in 1572. In these years, he collected some of the best designs, like Schwabacher and Fraktur, for which he is accredited to have cut a set of his own. He also possessed a number of matrices, which is a bit of a mystery since the punches for striking them were in the Plantin collection. Nevertheless, it is also to be noted that Sabon was awarded Imperial privileges in 1575 for casting five sizes of large format Fraktur alphabets. In 1578 another privilege was given to Sabon for the production type cast in copper, brass or bronze (Meldau, 1935). The document stated that using type in copper or an alloy enabled further use of these items after the pages were set. However, it is unclear exactly what this means. There are two possible hypotheses: the first is that the copper (brass or bronze) type was pressed into 'sand' (could also be a fine clay) to form the lines as sentences. On this 'sand', one or more lines were cast upon with type metal. The second option is that negatives of the punches were cast (as matrices), after which they were arranged to form the lines, upon which the type metal was cast to form the standing type. Sabon died in Frankfurt-am-Main between 1580 and 1590.

1.3.2.9 Jacques-Francois Rosart

Rosart was born in Namur in 1714. He appears to be self-taught and he started work in Haarlem in the Northern Netherlands. In 1741 he published his first type specimens. He also contributed many types to the Enschedé foundry, which had started in Haarlem in 1743. An advertisement in a Brussels newspaper introduced a new chapter in his life. He died there in 1777 (Macmillan, 2006). Described as typical mid-18th century Dutch style, Rosart's faces are sharp and light. Three sets are attributed to him (MA 45, 46 and 151) (Parker & Melis, 1960).

1.3.2.10 Johan Michael Smit

Smit worked for the Moretus family in Antwerp from November 1732 until April 1736. He was a punchcutter, mostly updating older Romans to the 18th century style (Parker & Melis, 1960).

1.3.2.11 Jean Baptiste Van Wolsschaten

Not much is known of Van Wolsschaten except that he belonged to a family of Antwerp founders and cut a Roman face around 1760 (Parker & Melis, 1960).

Further biographical information on other type cutters and strike makers from the 16th to 18th century, working for the Plantin-Moretus family or supplying printing material, can mainly be found in publications by Carter, Voet, Vervliet and Lane (see Bibliography).

1.4 The production of type

Type alloy compositions have often been a point of discussion in typographical research, and often seem to remain unclear from a metallurgic point of view. The greatest unfamiliarity is to be found in the first century of handpress book-printing, namely the period 1450-1550. Only very few type pieces from that period have been preserved, hence the information from that period is scarce. For the second half of the 16th century and later periods, only isolated type pieces have been analysed, leaving quite a lot of room for interpretation. The alloy compositions do, however, seem to be very important in establishing conservation directives, especially where the development of corrosion is concerned.

The following chapter is dedicated to existing literature on the production of type throughout the 16th to 18th centuries and includes information from the most important contemporary texts on type alloys: Vannoccio Biringuccio's La Pirotechnia (1540), Joseph Moxon's Mechanic Exercises on the Whole Art of Printing (1683) and Pierre-Simon Fournier's Art typographique (2 vols., 1764-1766). Furthermore, some shorter texts are included on the topic, and finally the information and techniques from these documents are examined in the light of the notes and comments of three more recent authors. Harry Carter (Carter, A view of Early Typefounding up to around 1600, 1960) had some of the assumed sixteenth-century types in the Plantin-Moretus Museum collection analysed, while Leon Voet (Voet, 1969-1972) looked into the archives of Plantin-Moretus. Walter Wilkes (Wilkes, 1990) discussed the characteristics of the different components and those of different alloys using them in different combinations. As a comparison, results from analytical measurements on types from other collections have been added.

1.5 Alloy compositions

From historical literature, analysis of historical objects and from practice, it is known that alloys for printing letters come in a very large variety. The base metal is lead in all known cases, and the primary hardening element is antimony. In many examples tin is added too, while copper and iron are found in smaller amounts or traces. In some exceptional cases, silver, bismuth or gallium was detected.

1.5.1 Early type alloy compositions

There is little known about the very first alloys used for casting type in the mid-15th to mid-16th century. We do know however that the reproducing and casting techniques are derived directly from the art of goldsmithing and the related art of the pewterer*. It is known that Gutenberg was involved in the mass production of pilgrim badges before he developed (or is said to have developed) movable print. The direct and causal relationship between these two forms of culturally important mass production items has already been mentioned (Köster, 1983). A copper die-piece in the British Museum showing the surviving half of a Wheel of Fortune is proven to have been used for the production of identical brooches in precious metal. An identical pewter fragment held in Zierikzee is a cheap cast version probably made with the same English die-piece (Ramsay, 1987).

Insignia, pilgrim badges or other religious and secular badges were very common in the early Middle Ages. They were usually cast in lead-tin alloys because this material was relatively cheap and very easy to produce in large quantities. These alloys produced pieces with the utmost fine details, leaving us many surviving examples from the 14th and 15th centuries (Van Beuningen, 1993) (Van Beuningen, Koldeweij, & Kicken, 2001) (Van Beuningen, Koldeweij, Kicken, & van Asperen, 2012). The most commonly applied technique was casting, although stamping or pressing could have been used too, either with or without a heating technique for open-work pieces. How the prototype was formed, and what kind of casting mould was used, varied from engraved slate over clay and plaster to sand or bronze counter forms. Van Beuningen describes the techniques used and the composition of 48 badges in his collection. Analyses revealed that 44 badges consisted of a tin-lead alloy, of which 24 had a tin concentration between 50-65 % and 13 badges were lead-rich with a tin concentration between 35-48 %. Five others were almost pure lead (96-98 %) and two were either pure tin or tin with 11.8 % copper.[14] The remaining four badges proved to be copper-based alloys (Van Beuningen, 1993). Many brooches were decorated with text or in some cases they were merely decorated letters themselves. With this existing tradition, it is understandable and very likely that this technology was transferred to the printing process with movable type as attributed to Gutenberg.

1.5.2 Historical sources for alloy compositions

1.5.2.1 Vannoccio Biringuccio (°c. 1480-†c. 1539)

The first text to disclose some of the knowledge about printing type and its alloys is to be found in the Italian Treatise La Pirotechnia by Vannoccio Biringuccio, published in 1540 just after his death. The content of this book was collected in the first quarter of the sixteenth century and is the oldest known source of information on the topic. Biringuccio had the opportunity of travelling through Italy and to Germany during his early years. He indicates in the text that he visited Friuli and Carnia in Northern Italy in 1507, after having travelled in Germany (Biringuccio, Venice, 1540). It appears that Biringuccio made a second trip to Germany between 1526 and 1529. In ‘The Seventh Chapter, Concerning the Art of the Pewterer’, Biringuccio refers to ‘*the art of making the letters with which books are printed, and the other is that of making the sheets from which organ pipes are built*.’ Further, he writes: ‘*The letters for printing books are made of a composition of three parts of fine tin, an eighth part of black lead, and another eighth part of fused marcasite of antimony.*’ In ‘The Third Chapter, Concerning Antimony and Its Ore’, Biringuccio mentions that ‘*from Germany they bring to Venice some of the smelted kind in cakes for the use of those masters who make bells, because they find that by mixing a certain part of it with the metal the sound is greatly increased. Those who make pewter vessels also use it as do those who make mirrors both of glass and of a special composition of metals.*’

It is indeed a known fact that the addition of metals that harden the alloy gives the bells a brighter sound. When metallic mirrors are produced, the addition of antimony can greatly harden the lead-tin alloy, which makes it much brighter and easier to polish to a high gloss finish for accurate reflections. As Gutenberg was also involved in the mass production of pilgrim mirrors, he might also have used this knowledge for his production, although there is no evidence for this. Unlike the wear and tear that occurs on type used for printing, pilgrim signs or mirrors do not suffer that much and could also easily be used and maintained without antimony in their alloy composition. Moreover, a precise date for the introduction of antimony in the 15th century cannot be given.

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[14] Note: The X-ray Fluorescence (XRF*) analytical technique used at the time, gave also arsenic (As) as a minor element (average of 0.9 %) in almost all measured alloys. This was considered to be a trace-element by the author and the researcher, but could also be due to overlapping peaks of Pb and As in the XRF-spectrum.

1.5.2.2 Joseph Moxon (°1627-†1691)

Moxon (England) opens his Preface with a description of different terms and working conditions. A first hierarchy is found in the distinction between the Master printer, who ranks first and the subsequent workmen: 2) The letter-cutter, 3) The letter-caster, 4) The letter-dresser (these three men are grouped as the 'Founders'), 5) The compositor, 6) The corrector, 7) The press-man and 8) The ink-maker (the latter four are grouped as 'Printers'). In assistance, there are other trades such as the (black- or copper-) smith and the joiner (woodworker).

Chapter 2, 'Of the Office of a Master-Printer', focuses on the terminology used amongst printers. One important name is 'The Printing House'. This could mean the house where the tools were actually present and the printer executed his work. On the other hand, a Printing House was also the collection of tools, needed for all aspects of the printing trade. Therefore, it was possible to remove a Printing House from a building, meaning that only the printing tools were taken out.

Moxon further states that the care taken when choosing appropriate letters lies in four facts: that the letter 1) '*has a true shape*', 2) '*be deep cut*; *for then they will Print clear the longer, and be less subject to entertain Picks'*, 3) '*be deep sunk*' in the matrices and 4) '*be cast upon good Mettal, that it may last the longer*'.

This *Mettal* is addressed in chapter 18, §2: '*Of making Mettal*', implying it is lead (Pb), hardened with iron (Fe). To make the iron fluid, an equal weight of antimony (Sb) and stub-nails (soft but tough iron) is molten together. A long and detailed explanation is given as to how exactly these metals should be melted and poured together, showing a very difficult process which is vulnerable to mistakes or mishaps. Here, only the ratios of composing the alloys is taken in account. He takes an example in preparing five melting pots, each of a content between forty and fifty pounds, for which a new brick furnace is built. These melting pots are filled to the rim with an equal weight of iron and antimony pieces. The metals are molten until the workers hear '*bubbling'*, after which they continue to heat the fire to be sure all the metal is fully molten and homogenised. When molten, not more than a quarter of each melting pot is filled, i.e. about 10 pounds of the alloy 50% Fe: 50% Sb. Alongside, another furnace is built for the iron melting pots holding the lead. A ratio of '*about five and twenty pounds of Lead is taken for every three Pound of Iron*.' This seems to be simply a directive to know how much lead must be provided to melt and proceed. When all metals are in a molten state, lead is poured into each of the melting pots containing the iron and antimony alloy until they are full. To the ten pounds of Fe-Sb alloy, between thirty and forty pounds of Pb is added, leaving a composition of between Pb-Sb-Fe 80.0-10.0-10.0 and 75.0-12.5-12.5, without taking into account losses due to oxidation or evaporation.

A facsimile reprint of the original book was edited (Carter & Davies, 1978).

1.5.2.3 Pierre Simon Fournier (°1712-†1768)

Fournier (France) also devotes a complete chapter on the composition of the alloys in his publication (Fournier, 1764). The Chapter '*Du Métal servant aux caractères*' first goes into the overall composition. In a following chapter, he focusses on the antimony, which he calls '*Le Régule*'.

The alloy, used for casting letters, is a composition especially designed for this purpose and used for nothing else. Lead is the base, which can be reinforced or hardened by adding other metals or mineral ores. This is called matter (‘*la matière*’), with a distinction between strong matter (‘*matière forte*’) and weak matter (‘*matière faible*’). This matter has long been composed by using lead, rude copper (‘*potin’*) and sometimes iron: the latter are melted separately from the lead with antimony and then mixed. This is very hard and dangerous work (as Moxon also describes) and delivers only imperfect material. It flows greasy and thick and gives nothing but trouble when heating in the melting pan, because it forms hard and thick crusts on the melt, sometimes up to a fifth or sixth part of the complete melt.

It appears that, from the beginning of the 18th century, the work is simplified and enhanced by simply using lead and antimony (‘*de régule d'antimoine'*). ‘*Le Régule*’ is the refined antimony from its ore, obtained by removing earth parts, sulphur and salts by reducing it on a fire until bright metal parts remain. The ratio of antimony in the alloy is fifteen, twenty or twenty-five pounds (‘*livres'*) per hundred pounds of lead. In weight percentage this means respectively alloys with 13.0%, 16.6% and 20.0% of antimony. The three alloys are called weak, medium and strong matter. The highest content of antimony should be used for the smaller letters, i.e. ‘*Nompareille'* and ‘*de Mignonne ou Petit-texte'*. The respective melting points of the above-mentioned alloys are 275°C, 295°C and 330°C. The main reason for adding more antimony to cast smaller types would be a lower viscosity of the high Sb-alloy, in addition to a greater hardness. Fournier further states that old lead is preferable to new, because it is ‘*more purified and harder*’. New lead, such as mined in Bretagne (i.e. mid-18th century), is much too soft for this kind of application. Old lead may also contain some tin or other metals, making it harder. This is however in contradiction to Fournier's opinion that it is ‘more purified’. The lead, which is reinforced and hardened by the use of *Régule*, results in a metal that is dry and brittle. With the stroke of a hammer on an anvil, it easily breaks into pieces. The fracture surface presents fine and shiny grains. Melting antimony and lead together provides an alloy with a lower melting point than lead itself, according to Fournier ‘*because it is more porous and enables the heat to access more easily*.’ The molten mass loses weight and quality of use due to oxidation formation on the melt, which has to be removed every time a new scoop for casting is taken.

Fournier addresses separately the preparation and use of antimony. He states that the exact use and composition for the casting of letters has long been a secret, but because the alloy is now composed from lead and antimony, he decides to write about it openly in his work. The chemistry of the time only offers procedures for refining the metal in small doses, which is impractical for the commercial use of printing. Only one or two people in Paris were able to deliver the antimony to every user in France, making it a costly metal. Fournier himself developed the necessary tools and workflow at Orléans for the purpose of refining his own antimony.

As a historical comment, Fournier writes that the monk (‘moine’) Basile Valentin (°1394-†1450) used the mineral to cure his fellow monks, for whom he had no affinity, therefore he called the mineral-metal ‘antimoine’. Stibium (antimony sulphide) is found in several provinces of France, in Auvergne, le Poitou, and in Brittany, as well as in Germany, the Alsace and most of all in Hungary, which provides a great deal. As found, it is a dense and dark grey solid, and very fragile. The better ore is harder and heavier and reveals a large number of bright lines on breaking. It consists of a number of sulphuric parts, salts and oils, which make up about half of the mass. Fournier describes how the antimony should be reduced and purified from the ore, but this is not described here in detail.

A reprint and edited version of Fournier is published by Harry Carter and James Mosley.

1.5.2.4 John Smith (18th century)

Smith writes in his publication of 1755 that ‘*The composition of metal for Letter being various, and depending upon the discretion of the Founder, must needs have different effects upon Letter, and render it either more or less servicable*’. He further refers to Moxon, but adds about the German traditions that they used more than three ingredients that may consist of steel, iron, copper, brass, tin and lead, all which they incorporate with each other by means of antimony. ‘*This metal, if duly prepared, does not bend, but breaks like glass: it is harder than tin and lead; something softer than copper, and melts sooner than lead*’. From this passage it can be concluded that Smith was not a practitioner in the trade of typefounding since he describes the above type composition as breaking like glass, but being softer than copper, a contradiction in itself. The passage that says ‘*How they prepare Letter-metal in Holland, I have not learn'd: but from a certain instance (the narration whereof would require a long digression) I am persuaded that they differ both from the English and the Germans*’ may however serve as a clue to distinguishing regional uses of different type alloy compositions (Smith, 1755). A reprint of ‘The printer’s grammar’ was published in 1965.

1.5.2.5 Johann Gottlieb Cunradi (18th century)

Cunradi dedicated Chapter 25 of his book ‘Technologie oder kurze und fassliche Beschreibung verschiedener Kunste und Handwerker’ (Leipzig, 1785) to the art of making type in the chapter ‘Die Schrifftgieserey‘ (Cunradi, 1785). In this work, he writes about the composition for the casting of type ‘*…besteht aus Eisen, Antimonium oder Spieszglas, wavon das blaue hierzu das beste ist, und Blei, welche zusammengeschmelst warden. Kupfer und Messing sind noch besser als Eisen, aber zu theuer‘.* The composition seems typical for the 18th century and lacks tin as an alloying element. It is remarkable that he also mentions copper and brass (copper and zinc alloy) as alloying elements. *A* typical *(‘gewöhnlichsten*’) composition in this chapter consists of *‘5 lb Eisen, 11 lb Antimonium und 25 lb Blei. Ein drittel der ganzen Masse sen vermengtes Eisen, Messing, Kupfer und Zinn, zweidrittel Spieszglas und drei drittel oder die Helfste der ganzen Masse Blei.‘* The last sentence is believed to refer to the raw material that has to be put together, whereby an important percentage oxidises in the melting process and is lost. It could well be that the alloy that is produced in this way ends up with an approximate composition of the mentioned 5 parts iron, 11 parts antimony and 25 parts lead. In weight percentages, this would mean 12% iron, 27% antimony and 61% lead. Nonetheless, while the antimony content is very high but not unfeasible, the iron content seems unrealistically high. The making of this alloy is explained further: the iron is melted together with the antimony (because of the lower melting temperature) for one hour, which makes it stronger (‘*etwa nach Einer Stunde geräth es bei starker’)*. Meanwhile, the lead is melted in another crucible and then poured with a spoon of about 8 lb content, into the vessel containing the iron. The crucible is left on the fire until the melt boils and the desired degree of liquidity is reached (*‘So vermengt lässt man sie über der Glut stehen, bisz sie in dem Schmelztiegel aufkochen, den alsdann erst haben sie den gehörigen Grad der Flüssigkeit und die rechte Mischung.‘)* The most remarkable passage is however ‘Die Holländischen Druckereien hatten ehedem Lettern aus Silber, z.B. die Elzevirischen Edizionen sind Silberdruck‘, which when translated means that Dutch printers have silver letters whereas the Elzevier editions are silver printed.

1.5.2.6 L'encyclopédie de Diderot et d'Alembert (1751-1780)

The second volume that was published in 1752 describes on pages 650-663 '*Caractères d'Imprimerie*', printing letters. The text on page 655 reads: *'…de preparer la matière don't les caracteres doivent être fondus. Pour cet effet, prenez du plomb & du régule d'antimoine, fondez-les séparément; mêlez-les ensuite, mettant quatre cinquiemes de plomb & un cinquieme de régule; & ce mélange vous donnera un composé propre pour la fonte des caracteres. Ou, prenez de l'antimoine crud, prenez égale quantité de potin; mettez le tout ensemble avec du plomb fondu, & vous aurez une autre composition. La précédente est préférable à celle-ci, qu'il semble qu'on a abandonnée en France depuis une vingtaine d'années, parce qu'on a trouvé que le potin & l'antimoine faisaient beacoup de scories, rendoient la matiere pâteuse, & exigeoient beaucoup plus de feu. Au reste nous pouvons assurer en général que la matiere dont on fond les caracteres d'Imprimerie est un mélange de plomb & de régule d'antimoine, où le dernier de ces ingrédiens corrige la mollesse de l'autre.'*

The text reads that after the mould has been built and made ready for casting, the next operation is the preparation of the material from which the type will be cast. For this, lead and 'regulus of antimony' are molten separately after which they are mixed in a proportion of four parts of lead to one part of antimony to give a mixture suitable for type casting. Alternatively, crude antimony can be melted with an equal quantity of potin and mix with molten lead and you will have another alloy. Potin is a word that can have different meanings, but overall it is agreed that copper alloys are described. The text on the choice of the alloy depicts however that the first alloy is to be preferred because the one with potin was abandoned in France for the last twenty years. It was found that this mixture gave too much slag on the melt and made the alloy turn pasty an requiring much more heat to melt and cast properly. The final sentence states that type is cast in general from a mixture of lead and 'regulus of antimony', whereby the latter corrects the softness of the lead.

1.5.2.7 Unknown Dutch publication (assumed to be 19th century)

The Dutch publication 'Letterspijs' gives information on the composition of the metals for casting letters. It greatly resembles Moxon's description: '*Take a graphite crucible and put in 5 pounds tough iron nails and 12 pound of antimony to melt. When done, add 25-30 pounds of molten lead and stir well because the metals do not dissolve well. The hardness test is done by bending a letter. It should break fairly quick; if it bends too much, it is regarded too soft.*' He also reports that in the 'Bataafsche Republiek' (Holland, 1795-1801) copper (Cu) and tin (Sn) were added to the former alloy.

1.5.2.8 Oly (19th-20th century)

Oly writes down the compositions of the alloys, used at the 'Lettergieterij Amsterdam' in 1908, formerly 'N. Tetterode'. The ratios of elements for the casting of letters always consist of Pb, Sb and Sn, in variations between 62.8-82.5wt% Pb, 12.4-30.9wt% Sb and 4.0-8.3wt% Sn. For spacers, he proposes an alloy of only lead and tin in a ratio of 12.5 to 13.5 Kg Sn to 100 Kg Pb, or 88.5wt% Pb-11.5wt% Sn. He makes a distinction between Tea-lead ('*Theelood*') and Bloc-lead ('*Bloklood*'). From the given compositions, it seems that Bloc-lead is softer than Tea-lead because of a systematically larger addition of tin and antimony. He also mentions that for letter-metal a fixed ratio of Pb 63%, Sb 30% and Sn 7% is maintained.

1.5.2.9 Monotype manual (20th century)

The 'Monotype' casting machine manual (Monotype, 1960) offers some more recent alloy compositions. At first, an alloy of lead with 15% antimony and 6-7% tin was used. Later, when it also became possible to cast larger letters on these machines, a harder alloy was used: lead, 19% antimony and 9% tin. The workers tended to use this for all letters from that moment on. However, it was difficult to obtain full, i.e. not hollow, letters every single time. A slight alteration was made to the alloy and a new standard was used: 74% lead, 16% antimony and 10% tin. It also melted at a lower temperature and was even used for spacers and interlines.

Nevertheless, for special purposes other alloys were sometimes used: for reprinting or to include additions to timetables, an alloy of 70% lead, 17% antimony and 13% tin could be appropriate. For larger letters ('*smoutletters*') of 14-36 points a very hard alloy of lead, 24% antimony, 12% tin and 0.5% copper was recommended.

1.5.2.10 Harry Carter (°1901-†1982)

In 1960 Harry Carter published A view of Early Typefounding up to Year 1600 (Carter, 1960). On page 21 he states that the modern standard for foundry type is approximately 15% tin, 25% antimony and 60% lead, with a trace of copper added. Metal from historic types of Plantin was sampled and was shown to contain 82% lead, 9% tin and 6% antimony with a little copper. Type at that time found in Moravia (Czech Republic) and dating from a similar period to Plantin contains much more tin, i.e. up to 18% in one sample. Carter also mentions that for smaller type more tin is needed to establish a higher fluidity to fill the narrow moulds. He further introduces five references of tin letters that would have been used from the mid-15th to mid-16th century. He doubts however that tin was in fact used for type since it is too soft for small types and claims that tin and antimony are needed to produce the characters faithfully. Failure to achieve the fusion would explain the starved look of many early typefaces, according to Carter. He finishes this chapter with the mention of '*Gutenberg, while he was experimenting in Strasburg, bought lead*'. However, this is not evidence that Gutenberg used lead-based types. Lead was used for many purposes in a metal studio and could be used as auxiliary material, to be fused with tin to produce pilgrim badges or to mix it with tin (and possibly other metals) to produce type.

1.5.2.11 Leon Voet (°1919-†2002)

Research on this topic, executed by Voet in the 1960s and 1970s, also goes into the technical aspects of the letter founding at Plantin-Moretus, Antwerp (Voet, 1972). This publication derives detailed information from the archives held in the Plantin-Moretus Museum (MPM). Sixteenth-century records in particular are searched on all aspects of the printing trade of Plantin. He opens the chapter 'The Printer's Techniques and Methods' on the moulds and their value to the market. With regard to the alloy composition of the type, Voet refers to Carter where some analysis was made of letters from the MPM collection (Carter, 1960).

From the archival information, one can conclude that Plantin only used two terms to describe different qualities of casting alloys: '*estoffe*' or '*matière*' and '*estoffe*' or '*matière dure*' or '*forte*' on the other, without further elucidation. Voet assumes that the '*estoffe dure*' was made almost exclusively on the basis of lead with a strong concentration of antimony (i.e. without the separate addition of tin); whereas tin was added to the 'estoffe'. He quotes extracts from the archives to support this view (Voet, 1972). A text dated 1565 actually states how much of each ingredient Plantin needed to produce a given quantity of type-metal: 493 pounds of lead (63.8%), 155 pounds of antimony (20.0%), 100 pounds of tin (12.8%) and 25 pounds of copper (3.4%), making a total of 773 pounds. However, from this amount, only 517 pounds of usable type metal could be made, which means that about one third was lost or expelled during smelting. This was stated by Plantin himself in 1575 when he expressed his surprise to Hendrik van den Keere, who prepared type in his commission. From the 3027.25 pounds of metal he delivered, he received only 2713.50 pounds of type. The amount of waste material – the *lycagie* as it was termed — was much larger when iron scrap was added to the molten metal. Moretus noted in the 18th century for himself that most of this iron, together with a considerable portion of the antimony was lost during smelting. This is written in the 'Memorandum by Jan Michiel Smit'. Smit's proportions for the preparation of type metal includes old type to comprise half of the mixture to obtain good results: old type 50 pounds (30.5%), lead 50 pounds (30.5%), antimony 40 pounds (24.4%) and iron scrap 24 pounds (14.6%). In addition, compositions written down by Moretus himself show the lack of tin and copper, which were very expensive at the time (see Table 1.1). It has to be noted, however, that a certain amount of tin can be present in a batch of 'Old type' or 'Old lead'. The latter may consist completely or partially of lead came soldering points as mentioned in the archive notes, dating October 1563. These state that the printer bought 351 pounds of '*knoppen ou neuds de vieilles verrières à faire estoffe pour fonder lectres*', 125 pounds antimony '*pour faire l'estoffe dure à fondre*', 47 pounds '*estain d'Oostland* (tin from Germany) *pour faire matière à lectres*', 30 pounds of iron filings, 25 pounds of copper filings, melting crucibles and pots, etcetera. It is noteworthy that lead cames for stained-glass windows were also reused for the same purpose, although the soldering joints (knots, crossings of cames) had to be left out and could be sold for the purpose of letter casting.

Table 1.1: Cost of metal for composing type metal alloys.[15] Intrinsic value of the florin (fl.) declines between 1565 and 1760 roughly from 100 to 40.[16]

Cost/100 pounds	1565 Antwerp	1760 Antwerp
Lead (Pb)	3 fl. 18 st.	6 fl. 9 st.
Old lead (Pb +Sn?)		9 fl. 0 st.
Antimony (Sb)	5 fl. 8 st.	14-16 fl. 0-6 st.
Tin (Sn)	15 fl. 10 st.	
Copper (Cu)	17 fl. 10 st.	
Iron (Fe)	2 fl. 10 st.	1 fl 15 st.

Melting down was already customary in very early times: from about 1565 on at least, melting down old lead and alloys must have been a regular practice as described in the Plantin archives (Voet, 1969-1972). Moretus tried to keep up with tin and copper levels by remelting old type from Plantin's period, but after some time, the amounts of tin and copper became so low that they had little remaining functionality in the alloy. What has been preserved from Plantin's time consists mainly of exotic alphabets, which were used only exceptionally and were practically never recast.

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[15] (Voet, 1969-1972), p. 95-96.

[16] (Voet, 1969-1972), Annex 6, p. 440-445.

More on the acquisition of metals and the composition of type metal from the archives of Plantin-Moretus can be found in the publication by Voet (Voet, 1969-1972).

1.5.2.12 Walter Wilkes (20th century)

Walter Wilkes has published an elaborate work on all technical aspects of the letter forming and –casting process (Wilkes, 1990). On the composition of the casting alloys, attention is given from a metallurgic point of view. For the casting of letters, it is desirable to have a larger amount of tin-antimony crystals in the alloy because of their hardness. An alloy of Pb-Sb-Sn 79-15-6 wt% has a lower melting point but is harder than a binary alloy of Pb-Sb 85-15 wt%. On the other hand, for cost-benefit reasons, there are limits to these additions as well as technical specifications which demand specific alloy behaviour, such as in the case of certain 19th and 20th century casting machines. Examples of up to 28% Sb and 5% Sn are given. This alloy is also the standard DIN 16512 composition for the casting of letters (Hofmann, 1954). In this composition, tin-antimony mixed crystals occur next to pure antimony grains in the eutectic* matrix*. The segregation* of tin-antimony crystals is often a problem, in the melting pan itself as well as in the cooling of a casted piece. Antimony always has the tendency to rise to the surface, where it oxidises and mixes with other oxidation products, rendering it unusable and lost. On the testing of alloys, the letter-caster knows from experience whether the alloy is good or bad. He listens to the alloy while breaking a sample piece. This should break easily with a soft bang and the broken surface should look silvery grey and finely grained, like cast iron. Testing with a knife also gives off a certain sound, and the chip that comes off tells the workman whether it is still a good alloy or not. In ‘critical’ circumstances, chemical analyses are used. We can assume that the tests with breaking sounds and chipping with a knife were also used in previous centuries to evaluate the quality of an alloy composition. It is to be noted that bell-founders and bronze casters also use a similar method by giving a strong hammer blow to a bronze ingot. Hardness, grain structure, grain distribution and grain dimensions, together with porosity or inclusions, are easily assessed this way by experienced craftsmen.

On the subject of older use of alloys for the casting of letters, Wilkes writes the following texts from two publications, respectively from 1867 (Bachmann, 1867) and 1874 (Smalian, 1874), a time where hand casting was widespread and the first automatic casting machines were novelties. The most widespread alloy in use at the time was 75% lead and 25% antimony *regulus*, together ‘*with some pounds*’ of tin. ‘*The more pure the metals are, the better the alloy will become*’. On the quality of antimony it is said that the English kind is the best, in contrast to the so-called Westphalian, because of the percentage content of zinc. Hermann Smalian gives the following composition: 75 pounds of lead, 23 pounds of antimony and 2 pounds of tin. At that time, tin was only found in small quantities because of the price: when lead cost 100%, antimony was 400% and tin 1000%.

In the chapter on historical compositions for hand casting, Moxon, Krebs and Fournier are cited but no new information on compositions is given. The role of the formerly used iron is questioned, as to whether it could deliver the desired hardness or whether it was not lost due to oxidation and poor mix qualities in the lead-antimony alloy (Moxon, 1683) (Krebs, 1827) (Fournier, 1764).

1.5.2.13 Discussion

Concerning the use of antimony in type alloys, the hardening effect is unquestionable. However, many texts state that the addition of antimony resulted in an expansion upon solidification of the alloy in the matrix, thus leaving the most accurate reproduction possible of the casted letter. It is an accepted fact that antimony expands upon solidification from the liquid state, as does bismuth and water. In type alloys however, there is not sufficient antimony to benefit from this effect. At least 75% antimony should be present with the lead or lead-tin to have this effect (Thompson, 1930). These high concentrations are never found in type metals since they would be too brittle. Moreover, the melting point of these alloys (about 600°C) would be too high to handle and to cast in the copper matrices. Moreover, such high temperatures would promote oxidation of the copper matrices leading to a possible loss of letterform accuracy. As a result, type metals with low antimony concentrations do retract, but to a lesser extent than pure lead or lead-tin alloys. On the level of type dimensions, this shrinkage is negligible. The greatest benefit has to be found in its very low surface tension and low viscosity. These physical facts guarantee the caster accurate reproductions of the letters from the matrices.

1.5.3 Analytical research results on historical types

From historical literature and from analysis of historical objects, it is known that the composition of type alloys may vary considerably. Generally speaking, 16th-century alloys (in Antwerp) were presumed to consist of lead, antimony, tin and some copper and iron traces, evolving to lead-antimony-iron alloys (in 17th-century England, as described by Moxon). Towards the 18th century, the use of lead-antimony alloys (see Fournier) with very small amounts of tin, copper or iron were preferred, presumably because of the high prices for tin and copper.

1.5.3.1 Archaeological findings

At a printing shop, type could be cast whenever the matrices were available. This was usually done when fresh types were necessary after the older fount had worn down. This fact makes it difficult in many cases to link type with any certainty to a specific period in time. In this respect, the present known archaeological finds from the 15th to the 16th centuries such as in Lyon (France), Wittenberg (Germany) and Kralice (Moravia, Czech Republic) are prime artefacts upon which to perform analyses. They are discussed first as an introduction to the types from the MPM collection.

1.5.3.1.1 Lyon, France[17]

The left bank of the Saône river in Lyon, more specifically the area called ‘La Pescherie’, has been the home of goldsmiths since the 15th century. The first printers, who are considered to be the former founders, were also located in the same area. Between 1868 and 1869, printing type was discovered in the river by golddiggers filtering mud from the river. The types were first exhibited at an exhibition put on by the ‘Cercle de la Librairie’ in 1880, Paris. The subtitle for the types was ‘Lyon – Caractères d’imprimerie des XV° et XVI° siècles, trouvés dans le lit de la Saône. – M. Claudin – 73’. A second part of about 20 type pieces, mostly from the 15th century, is from the collection of G. Brassart and was shown in 1948 at the ‘Exposition du Livre Lyonnais’.

The most remarkable feature of some of these types is the pierced holes, as shown in Fig. 1.7 (upper right; lower left is a casting defect) and Fig. 1.8. These holes could have been used for a leading thread after composition to prevent loss during handling and printing. (Mosley, 1995). In the case of the loose type that was left on the printed page, it proved not to be functional or it was not used in this way.

Concerning the composition of these types, only very limited analytical measurements were performed on pieces from five groups and the results were published by M. Audin in 1954. The analytical instrument used was an Arc spark Quartz Optical Emission Spectroscope giving a spectrum in the range of 2250-4050 A. The results are formulated as follows:

1. The five types all consisted of a ternary alloy containing tin, lead and antimony.
2. Pieces 1, 4, 5 contain a small amount of silver; pieces 2, 3 do not.
3. Type piece 2 is the richest in tin; the spectrum of 3 is too weak while the spectra of 1, 4, 5 are similar to each other.
4. All the pieces also show a small quantity of iron.

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[17] (Audin, 1954), p.85-92

Concerning the iron in the types, the comment which is given considers it to be an impurity from the metals that were used to compose the alloy. This is probably correct since we know that antimony is reduced from its ore using iron. The following comment that this could come from the casting in the instrument is doubtful. It is very unlikely firstly that sufficient amounts of iron would come off the ingot walls and secondly that these traces would remain at the surface after thorough handling and lying in the river for some centuries. If the iron proves to be a surface phenomenon, it is very likely to be a deposit from the river bank. As a net result, we have to conclude that the low iron content is none other than traces from the antimony in the alloy. This is certainly the case when destructive analytical techniques were used to measure all elements in the bulk composition of the sample, discarding any surface layer phenomena.

The conclusions given were that '*the alloy that was used by the first printers is identical of quality to the modern (1950's) alloys, that the lead ore contained sometimes traces of silver and finally that there is a variation in alloys that can be attributed to the founders who make the alloys as they chose and find appropriate*'. It is regrettable that no numeric alloy compositions were given. The conclusion that the alloys were identical to 20th century alloys is too shortsighted, since the precise variation in the content of tin and antimony in the lead alloy is predominantly to define the quality of casting the letter and the hardness to withstand multiple printing sessions.

Although new measurements on these types would be highly beneficial, it was not possible to get access to the types. There are plans to measure these types in the near future, in order to compare them with the Wittenberg finds (below) and the type compositions in the MPM collection.

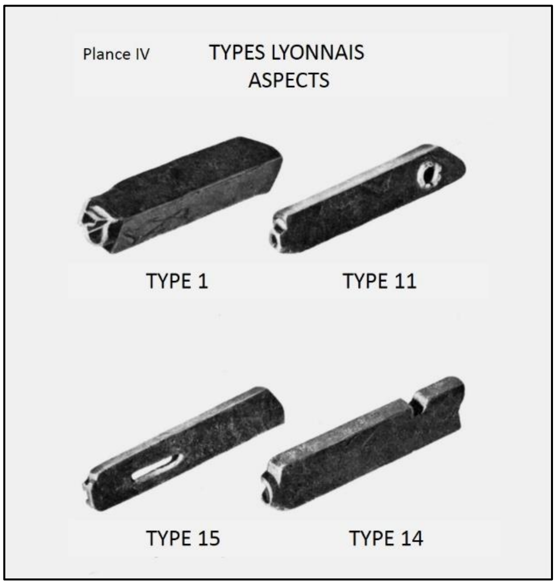

Fig. 1.7: Illustration of four type pieces from the Saône finds in Lyon.[18]

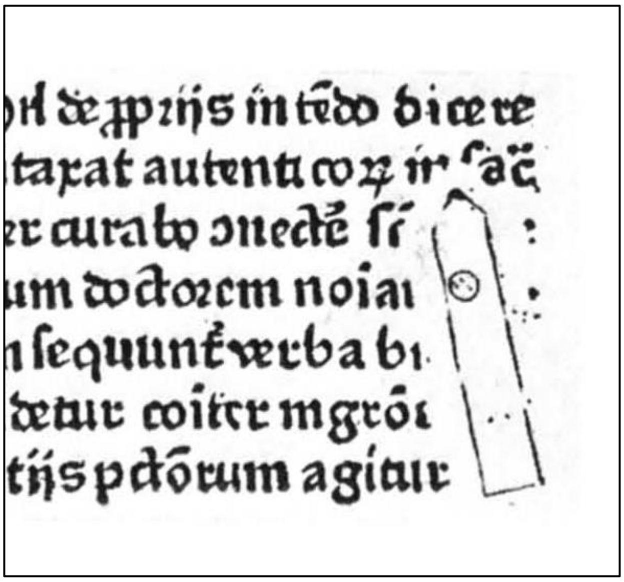

Fig. 1.8: An example of a type piece, drawn from the printing bloc, probably by the ink balls and left unnoticed while printing the page.[19]

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[18] (Audin, 1954, p.90)

[19] (Audin, 1954, p.87)

1.5.3.1.2 Wittenberg, Germany[20]

Recent measurements on archaeological type were performed by Dr. D. Berger (Germany) after excavating a complex at the Bürgermeisterstrasse 5 in Wittenberg. (Fig. 1.9) Several groups of movable type were unearthed in 1997 and 2011-2013. The adjacent archaeological findings date the types to the late 16th- early 17th century, which is also supported by their typographical characteristics. Other type discoveries from the 16th century were found at a former Franciscan monastery, the Arsenalplatz, the Juristenstrasse and the city church St. Marien. These findings represent up to 2700 pieces from Wittenberg. Average type alloy compositions were found to consist mainly of lead with a maximum of 12 wt% antimony and 8 wt% tin. More importantly and in contrast to other measurements, bismuth (Bi) is also present as an alloying element with concentrations between 1.5 and 2.5 wt% for the majority of the measured types. Because of this relatively high content, it cannot be attributed to trace from the lead ore. The Bi level seems to have a correlation to Sn and therefore is supposed to have been added intentionally as a separate alloy. Three main groups were identified: a first group of near-balanced amounts of Sb and Sn between 8 and 10 wt%; a second group with around 10 wt% Sb and 5 wt% Sn; and finally the third group with an inverted relationship of Sn and Sb. As stated earlier, the Bi concentrations often depend on the Sn addition and show in most cases higher values simultaneously.

Fig. 1.9: Type pieces found in the Bürgermeister-strasse 5 in Wittenberg during archaeological excavations. (Image courtesy of D. Berger)

Fig. 1.10: Corroded letters from Kralice. Top image: severe corrosion; bottom: slightly corroded. (Images K. Rapouch)

1.5.3.1.3 The Memorial of Kralice, Czech Republic[21]

The collection of Kralice types consists of archaeological finds since the printing shop burned down at the end of the 16th century, leaving types undoubtedly from that time. The Memorial of Kralice is one of the exhibitions in the Moravian Museum in Brno, the Czech Republic, situated next to the former fort where the secret printing house of Czech Brethren found refuge in 1578-1620. Not only books of religious character, for instance the very important Kralice Bible in six volumes, but also secular works and school books were printed there. Within the framework of the archaeological research in 1956-1958 the unique set totalling about four thousand different items of typographical material were

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[20] (Berger & Stieme, 2014)

[21] (Storme, et al., 2014)

studied, such as letters, spacers of type metal, bronze lines, etc. The form of the types is similar to that of the present day, belonging to the following fonts: Pearl, Nonpareil, Petit, Garamond, Cicero, Large text, Tertiary and Double large. The height of the type varies from 24.4 to 24.8 mm and their width varies from about 3 to 10 mm (Fig. 1.10). In comparison with the old Kralice printed books, the type can easily be identified and it can be shown that the find does belong to the 16th century (Fialova, 1959).

The results of the analyses performed by Dr. A. Selucka and colleagues (Brno, Czech Republic) show that the composition of objects in some cases differs significantly with regard to the content of lead and tin (Storme, et al., 2014). The two groups with severe and with slight corrosion seem however very similar in their mean composition of 79% Pb, 14% Sn, 6% Sb and 1% Fe. The iron content is attributed instead to the presence of corrosion products, since the letters were not cleaned for the XRF analysis. In general, the origin of the presence of iron in type metal may also be related to the method of obtaining the metal antimony from the ore through a process of melting and reduction of iron pieces.

The structure of the selected letters was evaluated by subjecting them to metallography and a scanning electron microscope with EDAX detector. The structure of ternary Pb-Sn-Sb alloys examined is shown in Fig. 1.11, which belongs to sample Nr.2265 with a chemical composition analysis of the cross section, giving a result of 67.3 wt% Pb, 20.0 wt% Sn and 12.7 wt% Sb. The structure of the alloy is formed by a light matrix (α phase - solid solution, mean values of point analyses: 8.0 – 3.5 – 1.0 wt% Pb-Sn-Sb), comprising fine grains of eutectic containing Pb, Sn and Sb. The structure also contains dark crystals of the intermetallic compounds Sn-Sb (mean values of point analyses: 0.0 – 56.0 – 44.0 wt% Pb-Sn-Sb).

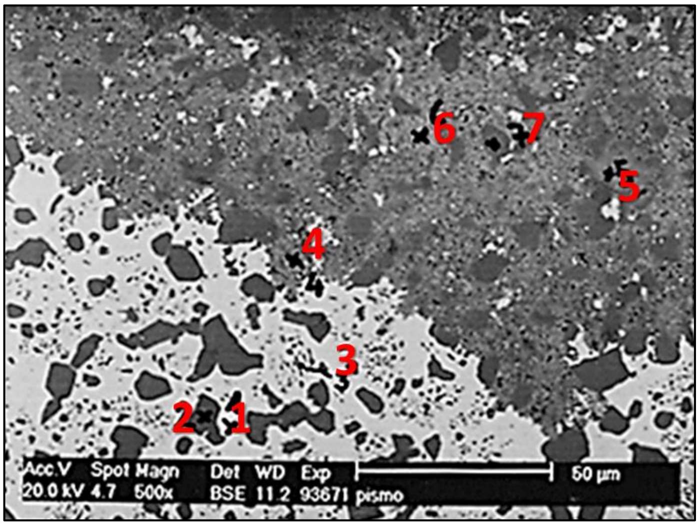

Fig. 1.11: Sample from the Kralice letter N°. 2265, in the unetched condition (SEM, BSE image, 500x).[22]

Location	Chemical composition (wt%)		
	Pb	Sn	Sb
1	97.0	2.9	0.0
2	0.0	57.4	45.7
3	15.4	47.3	37.3
4	72.9	7.4	4.3
5	80.0	2.6	0.7
6	81.2	4.8	1.4
7	0.0	56.2	43.8

Table 1.2: Chemical compositions of each phase (Points 1-7, see Fig. 1.11)

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[22] Image D. Janova, Faculty of Mechanical Engineering, Technical University in Brno.

1.5.3.2 Types from typographical collections

1.5.3.2.1 Plantin-Moretus Museum

Harry Carter (Carter, 1960) (Pelgen, 1996) shows analysis of Antwerp Plantinian lead type from about 1581, where it reads 82.71% Pb, 5.81% Sb, 8.99% Sn, 0.53% Cu and traces of Fe. This result is extracted from a small series of analyses that were performed in 1963 by the KIK-IRPA on the initiation of the director at the time, Prof. Vervliet, in cooperation with Harry Carter.[23] At the time three items were selected for analysis: 1) Drillings from the letter 'C' from the fount of '*Fort grosses capitales commencees Garamont*' (Parker, Melis, & Vervliet, 1960), which is an early serifed C made by J. Sabon in 1566 and which was replaced by another C by Hendrik van den Keere; 2) Drillings from the letter 'N' from the fount of '*Grosse Romaine Extraordinaire pour jecter en sablon*', which was supposedly casted by H. van de Keere; and 3) Filings of 6 letters 'e', dating from the 18th or 19th centuries. The analytical method was gravimetric for Sn and Pb, titrimetric for Sb and electrolysis for Cu.

Table 1.3: Results of the chemical analyses performed by the KIK-IRPA (Brussels, 1963) on three groups of items, dating from the 16th and 18th-19th centuries.

Item	Year	Chemical composition (%)[24]			
		Pb	Sb	Sn	Cu
1	1566-1570	82.71	5.81	8.99	0.53
2	c. 1570	82.29	5.91	10.01	0.14
3	18th – 19th century	72.50	16.86	7.82	0.03

1.5.3.2.2 Others

An exhibition in the British Museum and Earl's Court in 1963 (IPEX, 1963) was the impetus to perform a number of analyses on type from different collections. The catalogue mentions the following: '*The examples assayed were taken from founts at the Museum Plantin-Moretus and the University Press, Oxford, whose age is attested by documentary proof.*' The results are listed in Table 1.4.

Analyses on letters from Mainz (probably 17th century) with SEM-EDX at 25 KeV gave the following results: 73.0% Pb, 25.0% Sb+Sn, 1.5% Ga, 0.5% Cu and Fe in traces (Pelgen, 1996). What is remarkable is the presence of Gallium as a rare metal in this alloy. First described in 1875 as an element, gallium melts at 29.8°C. It is assumed that the element was introduced in the smelting and purifying processes of antimony and was not intentionally added to the alloy.

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[23] Letter from the personal archives of Prof. H. Vervliet.

[24] Although not specified in the document, it is assumed that percentage by weight (wt%) was meant.

Table 1.4: Results of analysis on lead types from a range of periods, selected from different collections. The metals in the alloy are expressed as a percentage, presumably percentage by weight.

Year	Attributed	Description	Pb	Sb	Sn	Cu
1580	Plantin-Moretus, Antwerp	Type (not specified)	82.71	5.81	8.99	0.53
1647	Nicholls, London	Arabic	89.40	7.55	2.90	0.15
1650	Luther, Frankfurt a/M	Schwabacher	89.99	8.80	1.30	-
1655	Nicholls, London	Arabic	87.70	7.10	5.20	-
1660	Amsterdam	Greek	91.50	7.50	0.10	T
1700	Robert Andrews, London	Black Letter	90.00	6.50	3.50	-
1738	Caslon, London	Etruscan	84.17	14.25	1.70	0.05
1760	Baskerville, Birmingham	Greek	85.50	14.00	0.50	T
1776	Caslon, London	Arabic	81.10	17.50	1.30	0.10
1794	Caslon, London	Hebrew	76.30	16.60	8.00	0.10
1805	Figgins, London	Greek	75.70	21.40	2.80	0.10
1841	Watts, London	Sanskrit	70.60	18.80	11.40	0.20

1.6 The casting

Moxon and his treatise ‘Mechanick Exercises’ (Moxon, 1683) is the oldest known source addressing the details of the craftsmanship of casting in Chapter 19, *‘1. Of Casting, Breaking, Rubbing, Kerning, and setting up of Letters.*’ He explains that the caster must first kindle the fire of coals before putting on the melting pan with the metal. He should consider whether to cast small-bodied letters, the fire must be very hot, sometimes red-hot to make the letter come. Taking the casting spoon, he strikes the surface of the molten alloy a few times to break the oxidation film on the surface and he can take some pure molten alloy to fill the spoon. Casting this content into the mould, he shakes at the same time the mould for the fluid metal to fill it completely up to the face of the letter in the matrix. The metal cools down almost immediately, so it can be thrown out of the opened mould onto sheets of waste paper, which are put on the bench for this purpose. If the letter is small, it requires a harder shake than a large-bodied letter. In some cases, it is so difficult to cast a sharp small letter that the caster is forced to put a little block of tin into his molten metal, which makes it thinner and consequently has a freer flux to the face of the matrix. This obviously changes the composition of the metal. He closes the mould again and moves onto a new cast. Moxon states that a workman casts ordinarily about four thousands of these letters in one day. Concerning the addition of tin to the lead alloy, it can be confirmed from personal experience to be true. The tin provides a smoother surface and a silver-like finish of the cast.

In his publication Fournier uses the same work flow as mentioned by Moxon, namely the cutting of the punches (‘*Taille des Poinçoins*’), making of the matrices (‘*De la Frappe des Matrices*’) and the casting (‘*De la Fonte des Caractères*’) (Fournier, 1764). The chapter on casting (*Précis de la Fonte des Caractères*) describes the cast iron melting pan, which is divided into two or three parts. This division allows different alloys to be melted (‘*différens degrés de force*’) and to place several workmen around the furnace. It must be noted that the use of such a parted melting pan also contributes to inaccurate alloy compositions due to spilling in use. The heat can be turned up or down, according to the needs of the casting work. The fluid metal is also taken with a spoon and cast into the ingot of the mould, after which the mould is moved rigorously upwards (‘*relève brusquement*’), allowing the metal to flow completely to the face of the letter in the matrix below. Then the mould is turned and opened for the casted letter to be thrown on ‘*crochets*’. This is done two to three thousand times a day.

Fournier also addresses the problem of ill-casting for the smaller types (‘*mal venir*’). Besides controlling the heat of the fire under the melting pan, the method of casting and the movement of the mould should be adapted to get better results. Casting the metal while holding the mould at a certain angle and/or casting in a certain corner of the mould ingot, should all improve the running of the metal up to the face of the letter in the matrix. However, large letters sometimes prove difficult or impossible to cast sharply as well, and in these cases the afore mentioned tips are ineffective. For these, he recommends taking a pumice stone (‘*pierre-ponce*’), grinding it to very fine powder, putting it in a folded cloth, and making a kind of bag with which to dust the ingot, leaving a whitish layer. It has been found that this enables the metal to pass better and delivers a sharp casted letter. This fine dust layer probably reduces the temperature shock between the liquid metal and the ingot. However, this is only a hypothesis.

The manual, provided with the 20th century Monotype casting machine(Monotype, 1960), also gives instructions for the proper handling of the molten metal. This is of direct use for the Monotype casting machine, but can very well be applied for hand casting operations too. An important factor is keeping the temperature of the molten metal high, so that all metals in the alloy stay molten and completely dissolved in each other. When cooled down by a cold wind over the melting pot or if too much new and cold metal is added, antimony (with or without tin) will form crystals that are much lighter than the molten lead, and that will rise to the surface to oxidise and form an insoluble crust. If this happens, the metal is lost from the original composition.

Moreover, in respect to the separation of metals from the molten alloy, it is stated that there are in fact two layers at the surface(Monotype, 1960). The top layer crust consists of the oxidation products, the slag (‘*droes*’), but at the metallic surface, right under the slag, there are the lighter antimony or tin-antimony crystals, floating on the heavier liquid lead alloy. With sufficiently high temperatures (370-400°C) and stirring, they can and should be re-incorporated into the liquid alloy before they oxidise in the crust and are thereby lost.

Another aspect is the mould temperature. Whilst in the Monotype casting machine, the mould temperature is controlled by water cooling, there was no such control for hand casting in earlier times. When casting approx. 3,000 letters a day by hand, the moulds would become warm, depending on the work speed, the cast temperature, the casted volume of the alloy, the ambient temperature, etc. It can be assumed that a certain equilibrium was reached after some time of working, at which the parameters of the casting temperature and the alloy were set to obtain continuously good quality type.

1.7 The mould or ‘the instrument’

Early appearances of the ingot mould for type are rare. The best-known image is that of Jost Amman, 1568 (Fig. 1.12). Here, a pyramidal-shaped object is shown, where the typefounder pours down type metal from the top using a spoon to scoop some molten metal from a melting pot in front of him. The shape of the ingot differs from later and better-documented ingot systems, which leads to speculation about its exact function. Some assume that the hole, seen on the spare ingots on the shelf in the above image, is to hold the matrix. This may be true, since it appears that the typefounder holds his thumb in this hole while casting the metal. It is also assumed from the way he grasps the form, that this is needed to hold two parts together (Reed, 1952). This would be logical, but no clear evidence can be derived from the woodcut.

Later moulds evolved from fixed-width models to versatile adjustable models that enabled the user to choose the height and width he desired for his printing works. A typical mould from the MPM is shown in Fig. 1.13. The matrix is held in place with a steel bent spring that allows the caster to quickly remove the matrix and the ingot from the two-cheeked mould and quickly replace the matrix again to cast the next type piece.

Fig. 1.12: Detail of the illustration by Jost Amman, showing a pyramidal mould (1568).

Fig. 1.13: A mould in the MPM collection, shown upside down, with the steel spring that holds the matrix in place.

1.8 The matrix

1.8.1 Introduction

In handpress printing, several stages and multiple tools are needed in order to achieve an impression on paper. First, a design for a character is made, bearing in mind the style and dimensions required (size, body or x-height of the letter). A complete alphabet consisting of capital letters, lower case letters, numbers, accents, etc., is called a 'polis'. The main groups of styles (typefaces) are Blackletter, Roman and Italic.

Secondly, each character had to be cut in steel to obtain a 'punch' of the mirror image of the letter or character. This steel punch was then hardened and driven into a copper rod by striking it with a hammer. This imprint in the copper produces the 'strike', which has a clear negative shape of the punch. However, the force used to drive the punch into the copper produced deformations on the upper face and the sides, because of the plasticity of the material. To make the strike suitable for further processing, it then had to be 'justified'. The justification process involves filing down and smoothing all sides of the strike so that it fits into the casting mould, (also called the 'instrument'). The result of this process is called a matrix (see Fig. 1.19).

When all this has been done, the matrix is ready to be placed into the moulding tool and metal can be cast into it; this is called the 'type'. This casting process (typefounding) was carried out for each character, or letter, as many times as the printer expected to need this type for composing the pages of the book that had to be printed.

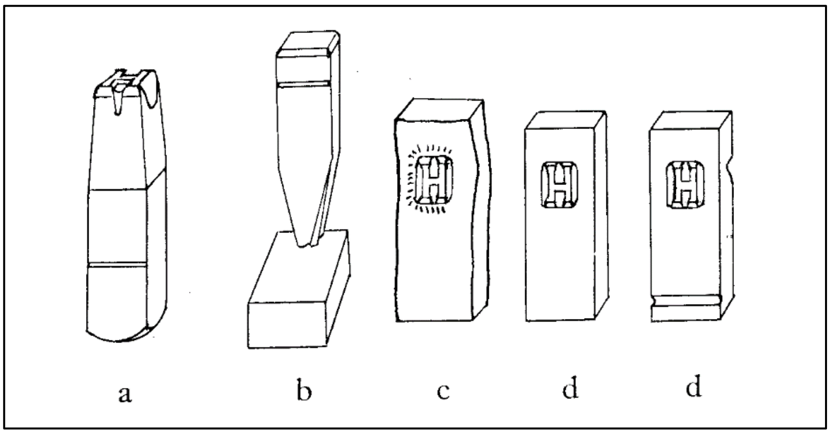

Fig. 1.14: The process of making a matrix with a) the steel punch, b) sinking the punch into a bar of copper, c) the imprint of the punch and the plastic deformations of the bar, d) justified and made to fit the casting instrument.[25]

1.8.2 Matrices use and trade

Matrices were a very valuable product and there was a lively trade between punchcutters/matrix makers and printers/traders throughout the ages of handpress printing. Whoever cut or owned the steel punches could produce a set of strikes. Most of the times, the strikes were sold to printers or type casters who justified the strikes to matrices fitting their moulds (instruments). Plantin himself was one of the most important buyers and sellers of his time. Anyone wanting to be the exclusive owner of a typeface had to buy the punches as well. Plantin sold large numbers of strikes to other printers. Twice a year there was a fair at Frankfurt where punchcutters and others gathered to buy or sell matrices. Frankfurt was a privileged place where goods could be stored as a deposit. Towards the end of his life, Plantin kept most of his punches and strikes there, probably as a safeguard against political or religious fluctuations. Plantin bought matrices for forty faces cut by Granjon, and often two or three, sometimes up to eleven sets of strikes. Guillaume Le Bé of Paris also made and sold matrices, just as Pierre Haultin had cut a Greek face that was sold to a German printer who probably also had it justified; it was bought by Plantin. In Antwerp, François Guyot justified matrices for Plantin and Ameet Tavernier sold three sets of matrices to Antwerp printers, one to Haarlem, five or six to Frankfurt and possibly

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[25] (Vervliet, Sixteenth-century Printing Types of the Low Countries, 1968), p. 7

some to Emden (Carter, 1960). There are records listing the sales of work by Garamond, Granjon, Le Bé and Pierre Haultin. But earlier, extensive trade throughout Europe was also likely (Vervliet, 1968).

1.8.3 Historical-technical aspects of the use of copper for matrices

Copper as a metal dates back to 9,000 years BC in Anatolia (Feneau, 2002) and found its widest practical use in the Bronze Age. In the Middle Ages copper was used in its unadulterated form for cooking utensils and also as a base metal for plating with silver or gold. In most cases, however, it was used as an alloying metal for bronzes, brasses, gold and silver alloys. The use of copper for making matrices in the context of hand printing is logical, when one considers the other metals that were available at the time. It has a high melting point (1083°C), is fairly soft (harder than lead, tin, gold or silver but softer than iron), has very good heat conductivity properties, is corrosion-resistant in ambient atmospheric conditions and is relatively cheap.

The processing of copper in the 15th and16th century is described by Biringuccio (Biringuccio, Venice, 1540). Chapter 3 in Book 1 concerns the localisation and mining of copper ore; chapter 4 is about refining operations. Chapter 8 of Book 3 goes into the parting of copper and lead from the 'matte', which is left from the assaying of silver. He mentions that the process leads to '*very pure and beautiful copper, which is called rosette* copper *and which comes from Germany in rough cakes*.'

In the second half of the 17th century, Moxon states in his work 'Mechanick Exercises' that '*The Steel Punches being thus finish'd, as afore was shewed, they are to be sunk or struck into pieces of Copper, about an Inch and an half long, and one quarter of an Inch deep; but the thickness not assignable, because of the different thicknesses in Letters…*' (Moxon, 1683). In the chapter 'Of Sinking the punches into the Matrices', he stresses the fact that the copper pieces must be large enough to enable the strike of long or wide formed letters. The coppersmith had to make rods of different sizes as the lettercutter would have instructed him by handing over wooden patterns that indicated the sizes he needed to produce successful strikes. He further instructs the coppersmith to choose the softest copper he can get, that the steel punches should not risk breaking upon striking. Moxon continues: '*The rose copper is commonly accounted the softest: But yet I have many times Sunk Punches indifferently into every sort of Copper. Nay, even cast Copper, which is generally accounted the Hardest: Because Copper, as well (as some other Mettals) Hardens with Melting.*' He also explains why the copper rods must be 'deep' enough: '*That the more substance of Copper may lie under the Face of the punch: For if the Rod have not a convenient depth, the Face of the punch in Sinking, does the sooner ingage with the Hardness of the Face of the Stake it is Sunk upon: And having with a few Blows of the Hammer, soon hardned copper just under the Face of the Punch, as well the hardness of the small (thus hardned) Body of Copper just under the Face of the Punch, as the Hardness of the Face of the Stake contribute a complicated assistance to the breaking or battering the Face of the punch. But if the Rod be deep, the Substance of Copper between the Face of the punch and the Stake is less hardned, and consequently the punch will Sink the easier, and deeper with less Violence.*'

It is certainly correct to observe that copper hardens quite readily under cold deformation such as striking with a punch. In the area being struck, the hardness increases from 45 to 90 Rockwell when reduced in thickness by 50% (Scott, 2011). Moxon continues saying '*But sometimes it has happ'ned that for the Sinking one Matrix or two, I have been loath to trouble my self to go to the Copper-Smiths,* *to get one Forg'd: and therefore I have made shift with such Copper as I have had by me. But when it has not been so deep as I could have wisht it, I have just entred the Punch into the Matrix upon the Stake, and to Sink it deep enough, I have laid it upon a good thick piece of Lead, which by reason of its softness has not hardned the Copper just under the Face of the Punch; but suffered the Punch to do its Office with good Success.*' Here, he points out that instead of an anvil, lead could also be used as an alternative base. The soft lead allows a deeper sinking of the punch even when the degree of localised hardness becomes too high to allow further deformation. This results in a deformation of the lower face of the copper rod but since all sides still have to be justified for use later, this poses no obstacle to producing a successful strike. It is worth noting that all the techniques described by Moxon appear also to have been used in the creation of the 16th-century matrices in the MPM collection. The copper sizes, the finishes, the justification, etc., seem not to have changed very much during the intervening century.

At the end of the 18th century, Fournier again describes a broadly similar process: '*Ce sont de petits morceaux de cuivre rouge, de quinze à dix-huit lignes de long pour l'ordinaire, sur trois lignes environ d'épaisseur, mais dont la largeur est relative à celle des lettres, des ornemens, &c. que l'on veut frapper'* (Fournier, 1764). Roughly translated as: Matrices are small pieces of red copper, fifteen to eighteen '*lignes'* long for the normal upon three lines thick, but the width is relative to the kind of letters or ornaments which are to be struck. In the 'Encyclopédie' a similar description is found in Chapter 2, page 653: *'…à former des matrices: pour cet effet il prend le meilleur cuivre de rosette qu'ill peut trouver; il en forme à la lime des petits parallelepipedes longs de quinze à dix-huit lignes, & d'une base & largeur proportionnées à la letter qui doit être formée sur cette largeur. Ces morceaux de cuivre dresses & recuits, sont poses l'un après l'autre sur un tas d'enclume…'* (Diderot-d'Alembert, 1751-1772). The text simply mentions the choice for the purest copper ('rosette') and the same dimensions for the copper pieces as Fournier describes. They are struck with the punches while resting on an anvil*, after they were made to the proper size and annealed*.

Regarding the kind of copper used, Fournier mentions that rods are cut from large '*plaquettes'* of red copper, called '*monnoie de Suède*' ('Swedish money'). These plates had a weight of six to eight 'livres' and each one bore at each of its four corners the arms of Sweden as a trade mark and also as a guarantee of its monetary value. After being cut into long rods, they were forged manually to an even thickness and to the desired dimensions. After the rods had been cut into smaller pieces to serve for the strikes, they were heated in a fire or kiln until they turned red, whereupon they were thrown into water to cool down rapidly. This made the microstructure more uniform and the copper overall softer. Fournier recommends this process only for the larger letters, so that they may be struck more easily. For the smaller punches, the slightly harder 'as cast' copper is sufficient, or even preferred, as it is more certain to retain the necessary strength and hardness after striking. To finish off the upper face that will receive the strike, it is filed flat with a coarse and a fine-toothed file, with a little oil being applied at the same time. The surface is then polished using a burnishing rod, which is a long, round and highly-polished steel rod. It is obvious that this method of finishing was also used on the 16th-century strikes in the MPM collection.

1.8.4 Matrices alloy compositions

From a metallurgical point of view, the copper used from the 16th to 19th centuries was not completely free of other metals, which were either already present in the copper ores themselves, or came from either the smelting and refining techniques or from the casting, hammering or finishing techniques used. For example, in pre-industrial times, copper was drawn from the ore by being heated (smelting*) and then refined using a combination of heat and oxidation. This process often left behind small amounts of lead and antimony. Since there were no more accurate scientific analytical techniques available at the time, the quality of the so-called 'pure' copper was tested by striking a cast test piece with a hammer while it was still red hot. If it stayed solid, it was considered pure, and thus suitable for further processing. If the test piece broke under the hammer, it had to be refined still further. This led to certain variations in composition. Although the copper was in fact not completely pure, it was sufficient for use in a variety of operations, not just for making matrices, but also for the production of sheets used for copper engravings or to support oil paintings as well as for alloying with precious metals (Scott, 2002).

Another consideration to take into account is the possible segregation of certain elements at the surface of a cast metal ingot. This is widely known as a surface enrichment, where in most cases the metal with the highest melting point solidifies first (in this case copper, 1084°C), making the detection of certain constituent elements with a surface measuring technique more difficult. In the case of the matrices, the copper content of 99 wt% or more ensures that the antimony stays dissolved in the copper grains. As can be seen in the phase diagram, antimony (melting point 817° C) forms an α-phase with the copper (Fig. 1.15, phase (Cu) left in the image). The highest dissolution is present at temperatures above 500° C (y-axis), diminishing with cooling down to room temperature (Sb concentrations on x-axis). With the very low levels (less than 1 wt%) that are to be expected in 'pure' copper, we can assume that all the antimony is kept in solution.

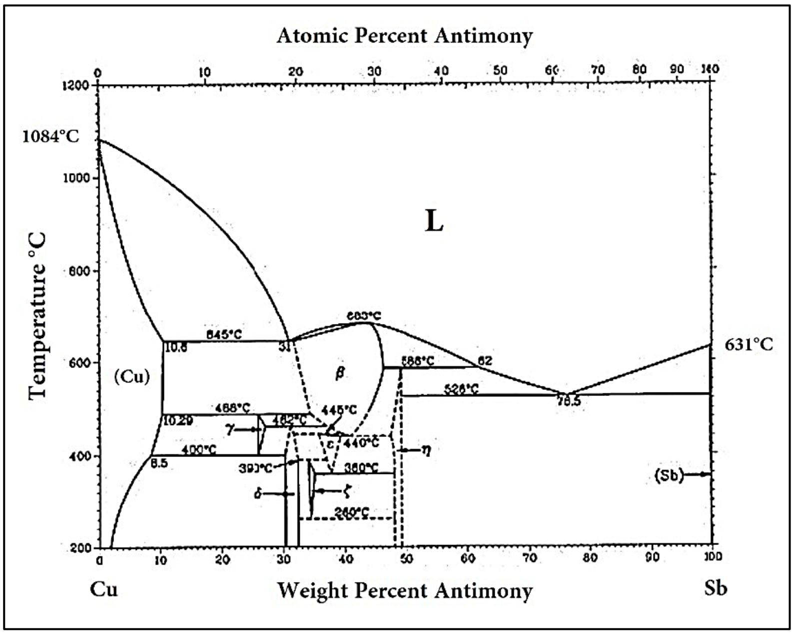

Fig. 1.15: Phase diagram of Cu-Sb.[26]

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[26] (American Society for Metals, 1990), Binary phase diagrams section

Lead, however, does not dissolve at all into copper (Fig. 1.16, no α-phase present) but stays as globules at the grain boundaries. Moreover, lead has the lowest melting point (327° C) and therefore solidifies last on cooling down from the casting. Other factors that can change the lead distribution in the copper are the annealing* and forging* processes that may have been applied to the copper rods. If this was the case for some of the copper rods (e.g. strikes and matrices), the initial lead content may have been re-distributed throughout the matrix.

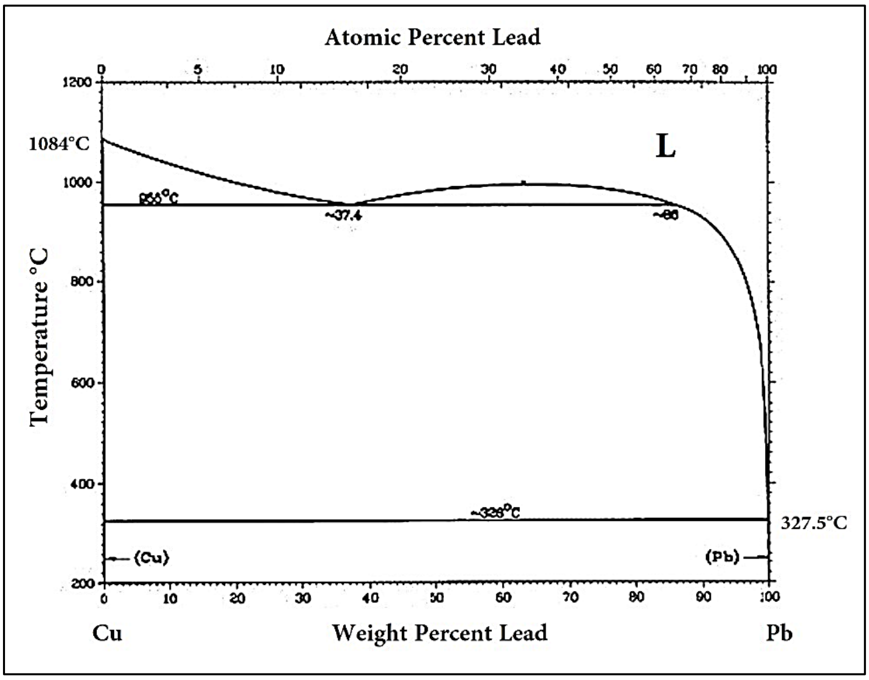

Fig. 1.16: Phase diagram of Cu-Pb.[27]

The possible segregation mentioned above must be taken into account since the measurements are performed at the surface of strikes (Fig. 1.17, Fig. 1.18) or on justified matrices (Fig. 1.19), where an important part from all sides has been removed mechanically. For the non-justified strikes, the measurements are taken at the upper surface with the punch mark, which was previously prepared to leave a smooth surface (Fig. 1.17) while the sides and bottom remained covered either with fire scale from the casting and/or hammering, or with saw marks (Fig. 1.18).

Fig. 1.17: The upper face and side of a strike.

Fig. 1.18: The side and back of a strike.

Fig. 1.19: Corrosion phenomena on some matrices in set MA 71.

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[27] (American Society for Metals, 1990), Binary phase diagrams section

However, more detailed information on the lead concentration and distribution throughout each strike or matrix could in this case only be obtained by destructive sampling and consequent analysing techniques such as metallography* or scanning electron microscopy (SEM-EDX), which are not suitable for the valuable historic objects currently under consideration.

1.8.4.1 Copper matrices

The majority of known matrices are made from copper. According to historic sources, the purest and softest copper was recommended to produce the strikes (Biringuccio, Venice, 1540) (Fournier, 1764). There is some discussion about the exact hardness required for the copper bars, whereas for smaller punches the absolute lowest degree of hardness was not considered strictly necessary (Moxon, 1683). From a metallurgic point of view, 'pure' copper can vary considerably in hardness. Besides the presence of some impurities, which can make the copper harder, the method of producing the bars for striking can also be very important for obtaining softer or harder copper. It has already been mentioned by Fournier that freshly cast copper is hard, meaning that 'worked' copper, which is hammered and annealed, gives a lower hardness and is therefore desired. Impurities in the copper originate from the copper ore itself, or from the way it was refined and prepared. The finest pure copper, as mentioned by Biringuccio, came from assaying silver alloys to pure silver, whereby the copper was divided in its purest way. This copper was called 'rose copper' (Biringuccio, Venice, 1540).

1.8.4.2 Brass matrices

Although struck brass* matrices are mentioned by Vervliet, most large bronze* or brass matrices are most probably cast (Vervliet, 1968). With reference to the account that Jérôme Haultin paid great sums of money to his uncle, Pierre Haultin, to acquire bronze matrices (Carter, 1960), it may not be certain that actual bronze was meant rather than copper. Bronze is much harder compared to pure copper or brass which would risk the punches being damaged. Sabon also mentioned having worked with copper alloys (i.e. brass or bronze), although in the imperial privileges that he acquired to use copper alloys in Frankfurt (Meldau, 1935), it is unclear whether punches, matrices or type was meant.

Brass matrices on the other hand have a hardness that in many cases accords with 'pure' copper. Moreover, brass has the advantage that it hardens less locally at the face of the punch. From a metal worker's point of view, it is surprising that brass was not used more frequently for the production of matrices since hardness cannot have been an issue. The lesser corrosion resistance or the wear and tear caused by casting type may explain why matrix makers persisted in using 'pure' copper.

1.8.4.3 Lead matrices

Lead matrices can be struck using steel, but also brass or bronze punches, as mentioned by John Smith referring to Mr. Struke, a printer in Lubec who ' *cut his punches in wood and sinks them into leaden matrices and even adds that the letters that were cast in these matrices were even deeper than the French generally are*' (Smith, 1755). This is uncertain from a technical point of view since lead is definitely very resistant compared to even the hardest kind of wood. It may be that the lead or lead alloy was heated just up to its melting point, which enabled the pressing of the wood model into the surface on which it solidifies. This process is also known as 'dabbing'. Making lead matrices from steel or copper-alloyed punches is possible by striking directly, or dabbing to obtain the major forms, and using a final strike to sharpen up the face in the cooled lead matrix.

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2 Metals, historical aspects and chemical properties

Content

2.1 Historical contexts

2.1.1 Applications of lead

Lead is a lesser-known metal for artefacts and objects; nevertheless, it plays a very important role in many applications.. Lead has played an important part in history: since Roman times water piping has been constructed from lead, building stones have been held together by iron fastened with lead, and lead slabs have been used to stabilise structures. Furthermore, lead was indispensable in precious metal work where it has been used since Greek times for cupellation* processes, purifying gold and silver by dividing them from lesser noble metals.

2.1.2 Architecture

Lead is traditionally used in architecture for roofing, piping, gutters, mending seams, ornamental pieces and sheet lining. Casting lead to hold iron clamps in stones or to position fences and statues is also a widespread application of lead. Stained-glass windows form an integral part of architecture. There, lead cames are have been used since early medieval times to fit the coloured glass pieces in the window composition.

The first historical references to the techniques used for the making and processing of lead cames are to be found in 'On Divers Arts' (Theophilus, 12th century) and Antonio De Pisa (14th century). Lead cames for stained-glass windows are known from Carolingian times, 8th- 10th century (Cuzange & Texier, 2000). The morphology of these very early cames is very basic and barely H-shaped. The cames have a width of 3.5-4 mm and a height of 7.5-8.5 mm. The soldering is very accurately and neatly executed. Numbering is found on the border in the form of 9 V-shapes (James, Trumpler, & Weyhe, 2000). The border lead is often doubled with the use of iron or wooden rods (Rauch, 2000) to reinforce the construction of the window glass.

Glass panels are normally secured in the lead came network using cement or putty. Often material remnants of a mineral composition, resembling a very fine cement, are found on the cames (James, Trumpler, & Weyhe, 2000). In the windows of Marienstatt yellow-brown remnants are found, of which 'leem' or clay is presumed to be the main ingredient, since there was an active ceramics industry in this area at the time. The high levels of humidity would pose no threat to this kind of compound for securing the glass in the lead net (Rauch, 2000). From a conservator's or researcher's point of view, a comparison with the corrosion issues concerning printing letters may be appropriate.

Lead cames are certainly considered important in the context of lead printing letters, since records show that lead from cames was recycled at the time the windows were replaced or restored. For the glassmakers only pure lead could be used to make new cames. Therefore, the soldering points from old cames were removed and collected separately to serve as lead-tin alloy for the making of type metal (Voet, 1966).

There has been ample research conducted on the composition over time. A good overview of the evolution of certain alloying elements in the lead alloy compositions is available on French window lead cames (Cuzange & Texier, 2000). Composition of lead cames in 13th-century windows is reported to consist of 99.1% Pb and 0.9% Cu (Rauch, 2000).

Contemporary lead cames are provided by a few companies, such as Heaps[1] and Stillemans[2]. The alloys are made of different qualities, often referred to as Extra-soft ('pure' lead), Soft or Half-soft, Medium or Half-hard and Hard. The variation in hardness is obtained by adding higher percentages of antimony, ranging up to about 1-2%.

2.1.3 Medallions, seals

Insignia, pilgrim badges or other religious and secular badges were very common in the early Middle Ages. They were mostly cast in lead-tin alloys because this material was cheap and very easy to produce in large quantities. The most commonly applied technique was casting*, although stamping* or pressing* could have been used too, either with or without a heating technique for open-work pieces. How the prototype was formed and what kind of casting mould* was used, varied from engraved slate over clay and plaster to sand or bronze counter forms.

In the chapter 'Technical Aspects', van Beuningen describes the techniques used and the composition of 50 badges in his collection (van Beuningen, 1993). Analyses revealed that one example consists of 95.9% of lead, 2.6% tin and 1.4% arsenic. The latter is attributed to pollution. Thirty-seven other pieces had higher tin levels, between 35 and 65%.

It is known that Gutenberg was involved in the mass production of pilgrim badges before he developed (or is said to have developed) movable print. The direct and causal relationship between these two forms of culturally important mass production items was mentioned by K. Köster in 'Gutenbergs Strassbuger Aachenspiegel-Unternehmen von 1438-1440' (Koldeweij). In the same publication, Koldeweij refers on p. 325 to a copper die-piece in the British Museum showing the surviving half of a Wheel of Fortune (in turn described by Nigel Ramsay in 'Age of Chivalry. Art in Plantagenet England 1200-1400 (London 1987) in the Exhibition catalogue[3]), which had been used for the production of identical brooches in precious metal. An identical pewter fragment kept in Zierikzee is a cheap cast version probably made with the same English die-piece (Koldeweij). Many brooches were decorated with text or in some cases were merely decorated letters themselves. In this existing tradition, it is very likely that a connection emerged between printing with metal pieces and the printing process with movable type, as attributed to Gutenberg.

2.1.4 Printing letters (type)

In the Eastern world, the very first use of metal (bronze) movable types is attributed to Korea during the Goryeo Dynasty around 1234. Hua Sui introduced bronze type printing to China in 1490. In Western typography, the introduction of 'movable type' in the mid-15th century was a very important technique at the junction of the medieval era and the Renaissance. Handwriting and copying could be replaced by a much faster way of spreading information and ideas, which contributed greatly to the evolution of society. Book-printing is regarded as an essential element of the Renaissance, the Reformation, the Age of Enlightenment and the Scientific Revolution, laying the material basis for the modern knowledge-based economy and the spread of learning to the masses.

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[1] http://www.heapsarnold.com/products/lead-came/ (consulted 15 May 2017)

[2] http://stillemans.com/upload/Lead%20cames.pdf (consulted 15 May 2017)

[3] Royal Academy of Arts, 395-6 cat. 450

Johannes Gutenberg (°1395 - †3.2.1468) is regarded as the inventor and founder of the use of movable type and the coalescent oil-based ink and screw driven printing press, around 1439. Moxon declares in his book Mechanick Exercises (Moxon, 1683) that he cannot ascertain whether Gutenberg from Mainz or Coster from Harlem was the true inventor of the movable metal type. He even states that Gutenberg stole Coster's tools while he was at church, took them to Mainz and promoted his claim to be the first inventor of this art. He also writes, '*About the year of our Lord 1460. The Art of Printing began to be invented and practised in Germany, whether first at Mainz or first at Harlem it is not agreed: But it seems that those who had it in consideration before it was brought to perfection, disagreeing among themselves did part Company; and some of them at Harlem, other at Mainz pursued the design at the same time*.'

The design of a suitable metal alloy and hand moulds for casting the types must have been developed simultaneously into a fully operational system, which was economical. There is, however, no accurate information available on the technical aspects of Gutenberg's practice. It is still a matter of debate whether Gutenberg or Coster from Holland was the rightful inventor of the system, although most academics today give Gutenberg all the credit. This discussion will not be continued in this work. However, it is important to note that historical information on this topic can be found in a 1568 history by Hadrianus Junius of Holland, the Cologne Chronicle of 1499 by Ulrich Zell and the Pirotechnia by Vannoccio Biringuccio, 1540. In addition, the 18th-century printer and typefounder Fournier Le Jeune commented on the conception of the movable type printing system. More on the representative figures for the history of printing will be addressed later.

2.1.5 Other applications

It is well known that lead and lead-tin alloys were used to make toys and models. 'Tin soldiers' are a good example. Furthermore, the casting of small ornaments for model ships was often performed with lead or lead-tin alloys because they had a low melting point and were easy to shape.

Lead sculptured statues appeared from the 15th century onwards, and became widely used from the 18th century (Ashurst & Ashurst). They often pose great problems for conservation, since the weak and heavy lead is normally mounted on an iron frame, which corrodes and causes the statue to collapse. Corrosion issues are reported too.

As regards weaponry, lead bullet ammunition was used from about 1500; the rounds, as they were called, were simple balls. The later evolution from flintlock guns to the revolver made it necessary to contain the gunpowder and the projectile in one unit. The so-called cartridge consists of a brass jacket that holds the percussion cap, the gunpowder and the lead bullet itself. Large quantities of lead are used in ammunition for both military and sporting purposes. These lead bullet points are often hardened with the addition of antimony. Alloys used for shot contain up to 8% Sb and 2% As; those used for bullet cores contain up to 2% Sb. Some studies have been conducted on the corrosion behaviour of those alloys in the grounds at firing ranges.

Grids in lead-acid electric accumulators (batteries) are made from lead alloys, as the pure metal is too weak; antimony is often added to improve the strength and castability of the alloy. Three types of alloys are widely used: 1) high antimony alloys, 4-11 wt%[4] antimony with traces of arsenic, tin, selenium, etc.; 2) low antimony alloys, 0.8-3 wt% antimony with some arsenic, tin, selenium, copper, sulphur, etc.; and 3) lead-calcium-tin-aluminium multi-element alloy. To increase corrosion resistance, additives can be used (e.g. silver) (Ghasemi & Tizpar, 2007).

Adding tin to lead alloys increases hardness and strength, but lead-tin alloys are more commonly used for their good melting wetting* properties, as with solder. Tin gives the alloy the ability to wet and bond with metals such as steel and copper; unalloyed lead has poor wetting properties. Tin combined with lead and bismuth or cadmium forms the principal ingredient of many low-melting alloys. Solders in the tin-lead system are the most widely used of all joining materials. The low melting range of tin-lead solders makes them ideal for joining most metals using convenient heating methods with little or no damage to heat-sensitive parts. Tin-lead solder alloys can be obtained with melting temperatures as low as 182°C and as high as 315°C. Except for the pure metals and the eutectic* solder with 63% Sn and 37% Pb, all tin-lead solder alloys melt within a temperature range that varies according to the alloy composition. The addition of cadmium or bismuth lowers the melting temperature even further.

Lead is also important as a shield against x-rays and, in the nuclear industry, gamma rays.

Lead cable sheathing extruded around electrical power and communication cables gives the most durable protection against moisture and corrosion damage, and provides mechanical protection for the insulation. Chemical lead, 1% antimonial lead, and arsenical lead are most commonly employed for this purpose.

Lead-base bearing alloys, which are called lead-base Babbitt metals, vary widely in composition but can be categorised in two groups: 1) Alloys of lead, tin, antimony, and, in many instances, arsenic; and 2) Alloys of lead, calcium, tin, and one or more of the alkaline earth metals.

Lead was also used as a source for mineral pigments such as lead white, minion, etc., for paints. It is also used as an element in crystal glass, which gives it a higher refraction index and therefore a greater brilliance.

2.1.6 Mining of lead

Lead does not occur in its native state. It is quite abundant in the earth’s crust at 15 ppm. Lead is mainly extracted from its ore galena (lead sulphide, PbS), from which impurities, like silver and bismuth are removed. It is also generally associated with silver, arsenic, antimony and bismuth (Costa, 2005). The silver content was in most cases the most important by-product from refining lead. The primary goal was often to extract lead in order to refine silver from the ore. Other minerals are cerussite ($PbCO_3$) and anglesite ($PbSO_4$), in addition to crocoite ($PbCrO_4$) which is a chromate with a fine red colour but without any economic value.

The description of lead and its products is addressed by Gregorius Agricola (°1494-†1555) in his work De Re Metallica (1556). He refers to eight variants of lead and lead substances and contributed only lead ochre as a new material. Before him, writers in classic times often confused lead products and

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[4] wt% = percentage by weight

designations, so that ‘plumbum’, ‘plumbago’, ‘galena’ and ‘molybdena’ applied to lead substances of indeterminate form (Dibner, 1958).

Another important source from the 16th century is Vannoccio Biringuccio with his work ‘The Pirotechnia’, published in 1540 just after his death (°1480-†1539). He addresses the properties of the ores, the smelting, the refining (Fig. 2.1) of noble metals using lead cupellation (Fig. 2.2) and the art of the pewterer*. Concerning the smelting* of ores, the melting* of metals and composing alloys, different chapters contribute to these fields. There were many ways to obtain metals with certain degrees of purity, depending on the ore composition and the installation at hand. It lies beyond the scope of this study to go into further detail on this matter.

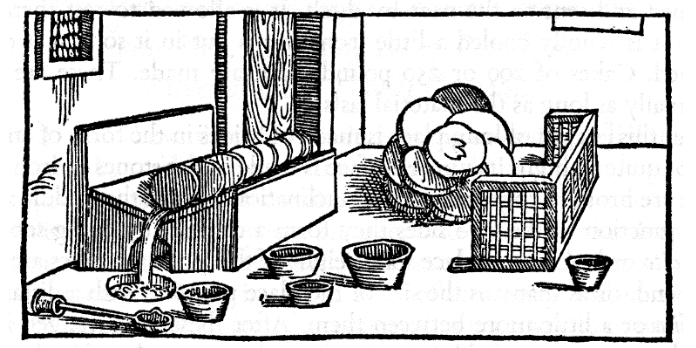

Fig. 2.1: Liquiation hearth for parting lead from copper cakes.[5]

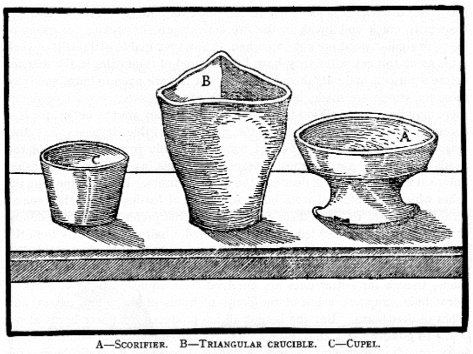

Fig. 2.2: Three types of cupels for parting noble metals from lead.[6]

2.1.7 Recycling

Lead is easily recyclable and the impurity content can increase every time it is remelted. It has been suggested that up to 10% of the lead in use today dates from Roman times (Walker & Hildred, 2000). Throughout time, the recycling of lead has been exploited. Examples are to be found in pipe organ building (Speerstra, J., 2011) and with lead typecasters who used scrap tin soldering points from renewed stained glass windows (Voet, 1966).

In the late 20th century, approximately 65% of the lead produced worldwide was not from ores but recycled. The low melting point and relatively easy refining process has been used since Greek times for the reuse of lead. The continuous re-use of lead makes identification of provenance very difficult when the lead product or object has not been composed directly from the primary metal extracted from the ore of a particular mine.

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[5] (Biringuccio, 1540)

[6] (Agricola, 1530)

2.1.8 Copper

Throughout history copper has been one of the most important metals and dates back to 9000 BC in Anatolia and 6000 BC in Iran. The first objects were manufactured by cold hammering of native copper. More extensive use in later periods was made possible by producing the metal from oxidised ores. In approx. 4000 BC the processes were commonly mastered and led to the Bronze Age. The most representative copper minerals from which copper is derived are: chalcopyrite, chalcocite, covellite, azurite, chrysocolla, cuprite and malachite (Feneau, 2002).

The Romans mainly used the copper from Cyprus, called Cyprium (Cuprum, Cu), hence the name. In the following centuries, many other places were explored, such as Saxony and the Harz region in Germany in the 10th century and Mansfeld, Germany, in the 13th century (Feneau, 2002). Sweden is regarded as one of the most important copper mining countries in Europe. The site of Falun is world famous and may even go back as far as the temple of Solomon. The first written proof dates back to 1288 (Neher, 1943). Arriving at the 15th century, when printing with metal matrices evolved, copper mines were present throughout Europe and abroad. In this period, England became an important rival to German copper mining (Neher, 1943).

In Germany, Saxony, silver and copper was mined intensively between 928 and 1423 in Biensdorf. From the 15th until the 17th century, there were a large number of small coppersmelting sites in the Vogtland and higher areas. It was noticed that the copper ore contained a sufficient amount of silver to be extracted and by 1493 almost all the Saxony copper was transported to the Grüntal area to separate the costly silver. In Hettstedt, later called Kupferberg, copper mining started in 1199. After the donation of privileges for mining copper from Emperor Frederik II to the Count of Mansfeld in 1215, the Duke and future Elector of Saxony became the 'opperleenheer' ('supreme lord') in 1466. In 1590, a new copper mine was created in Frankenberg near Kassel, where four years later a smelting facility was opened on the shores of the Edder. In the third quarter of the 17th century, copper smelting was performed at Leimbach and the silver smelting took place at Mansfeld. In 1723, a copper smelting facility was established in Hettstedt. Nürnberg became the centre of copper trading, with Fürer and his companion Dr. Drachstedt as an important personality. The monopoly they had ended in 1525 with the installation of a new smelting facility in Mansfeld, directed by Count Albrecht of Mansfeld. The first metal purification installation was set up in Leutenberg. The result was intense competition with the Fuggers, who also imported raw ore from Hungary. They shipped their copper to Stettin and later to Antwerp, one of the most important trading places for copper and other non-precious metals in 15th-century Europe. As opponents to the Fuggers who dominated in Hochkirch, the Augsburg' family Welser were together with Fürer the leading figures in the mines and smelting facilities of Leutenberg, Arnstadt and Mansfeld. Multiple intrigues and plots resulted in a cartel that was the first of its kind in 1534. In the meantime, Bartolomeus Welser was given the Province of Venezuela to colonise by Emperor Charles V. It was only until the first half of the 17th century, while German mining was suffering from the Thirty Years' War, that the mines in South America flourished. In the last quarter of the 17th century, Germany was able to recover from its destruction and a large number of independent mines were the result (Neher, 1943).

2.2 Chemical properties

2.2.1 Lead

Lead is a metal with a low melting point (327°C) and a relative high density of 11.53 g/cm^3 (Stegwee, Vaesen, & Van der Eyk, 1947). It is very soft, malleable, ductile and poisonous. With these properties, lead can be easily cast and alloyed with other metals. Lead is also very corrosion-resistant under a wide variety of conditions. Alloying with other metals, notably calcium or antimony, is a common method of strengthening lead for many applications. The addition of other metals gives the lead alloy a fine-grained structure, but this can also be achieved by any kind of deformation. It generally improves the mechanical properties as well as its resistance to corrosion in non-acidic environments (Costa, 2005).

Current grades are pure lead (also called corroding lead) and common lead (both containing minimum 99.94% lead), and chemical lead and acid-copper lead (both containing minimum 99.90% lead). Lead of higher specified purity (99.99%) is also available in commercial quantities. Specifications other than ASTM B 29 for grades of pig lead* include federal specification QQ-L-171, German standard DIN 1719, British specification BS 334, Canadian Standard CSA-HP2, and Australian Standard 1812 (Cardarelli, 2008).

2.2.2 Toxicity and waste

Lead is harmful for our environment. There have been many discussions on this issue and for a long time it was assumed that 5 g/m^2 entered nature over time. Research at the TNO has shown that in reality this is more likely to be 1 g/m^2. Many lead corrosion products are highly poisonous and easily distributed on hands, in the work space and in the air because of their poor surface adherence. Cerussite and hydrocerussite are amongst the most dangerous substances. Safety issues related to the matter of 'metal type production' include the poisonous fumes emitted while melting lead, and the particles and dust coming from sanding and polishing lead and lead alloy samples in this research. Since the highest toxicity from lead occurs from dust or fumes from melting, a number of precautionary measures were taken in different phases of the research. Fumes were extracted by melting in a shielded cabinet, whilst the remnants of polishing were collected in a filter and disposed of as heavy metal waste product. A comprehensive work by L. Selwyn looks at the risks of lead in conservation (Selwyn, 2005).

2.2.3 Lead alloys

Lead was often selected for its malleability and chemical resistance to corrosion, for use in water pipes, roofing and sealing material for iron stone bindings. Many other applications however required higher strengths and hardness values, while creep and melting points had to be lower. This is for instance the case for printing letters and organ pipes.

The alloying metals each have their specific influence on the chemical and physical behaviour of lead. Moreover, very small additions of other metals (i.e. in some cases even hundreds of percent) can completely change the microstructure of lead. The presence of a second phase by the addition of tin or antimony contributes to the production of a fine-grained structure that has important consequences for the properties of the lead alloy (Costa, 2005). A range of names was given to different 'qualities' of lead, as described in historic treatises. In many cases, impurities or small additions of other metals lay at the basis of these differentiated lead sorts. As an example, Plantin lists the use of 'old lead' for making type, while there is no evidence that tin was acquired or added. Nonetheless, it is known that old cames from glass windows were recovered for their soldering points, where tin was used in the solder (Voet, 1966)[Arch. 36, p. 64]. Hence, this was a lead-tin alloy, which was used for the production of types without specifications for the tin or its content in the lead alloy.

2.2.3.1 Lead-tin alloys

In addition to lead, tin is also frequently present in the alloys of the printing letters. Tin is a metal with a silvery-white colour; it is soft, malleable, non-poisonous and non-magnetic. Because its melting point is very low (232°C) and its low hardness makes it too soft for most applications, it is usually alloyed with other metals. The most common alloy is 'pewter', which in former times was a tin-lead alloy (70wt% Sn-30wt% Pb) and in modern times a tin-antimony alloy (Sb <10%).

The binary phase diagram of lead-tin alloys is shown in Fig. 2.3, where the minor solubility of both metals in each other is indicated (αPb and βSn). It forms an eutectic alloy at 61.9/38.1 wt% Sn/Pb, meaning that a molten alloy of this composition solidifies instantly, as opposed to other alloy compositions that show an intermediate semi-solid phase (α+L and β+L) before solidifying completely on the indicated solidus line (183°C). Because it also has the lowest melting temperature of all alloy compositions, it is often used as a solder.

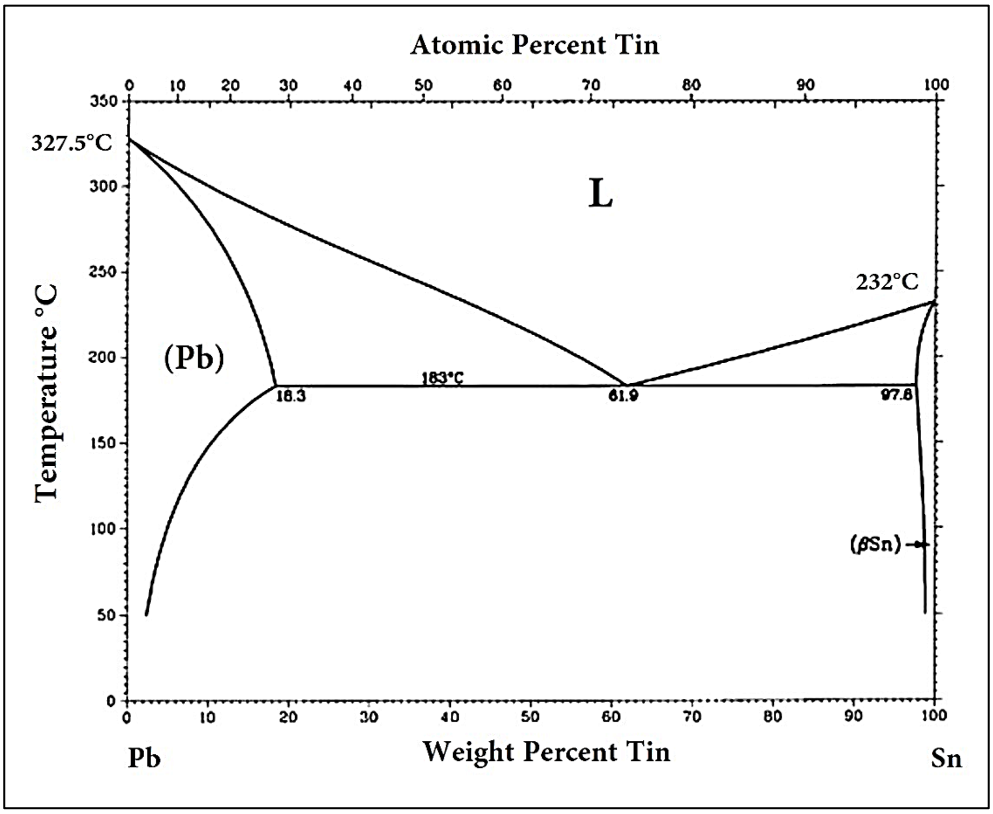

Fig. 2.3: Binary phase diagram of lead-tin alloys.[7]

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[7] (American Society for Metals, 1990), Binary Alloy Phase Diagrams section

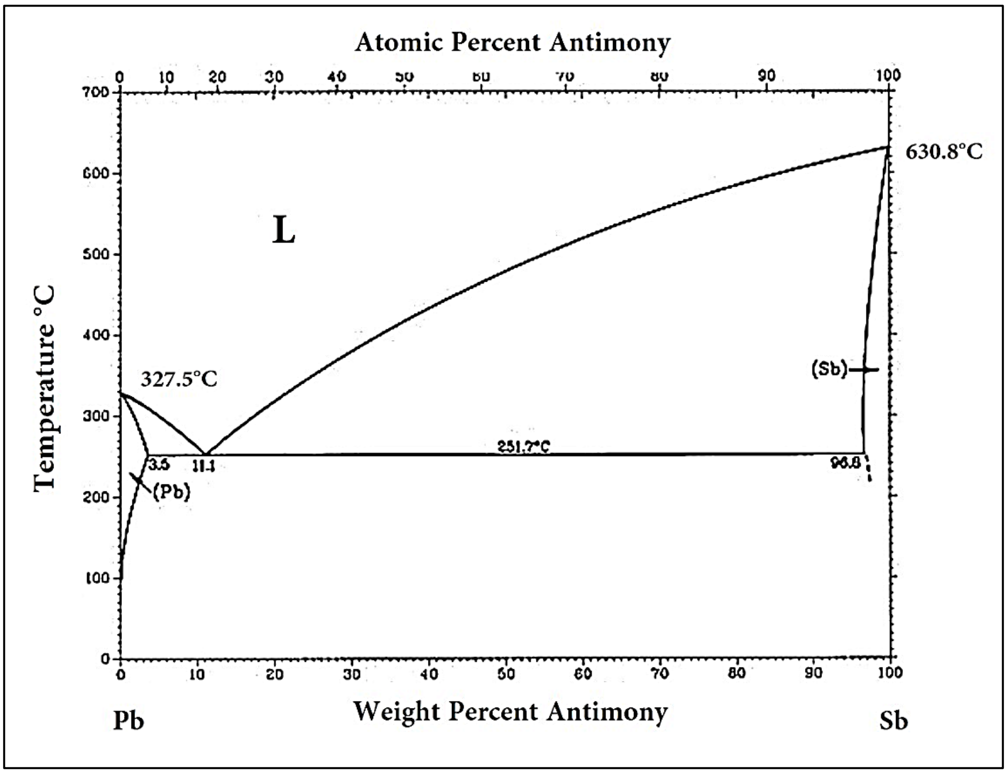

Fig. 2.4: The binary phase diagram of lead-antimony alloys.[8]

2.2.3.2 Lead-antimony alloys

Antimony is detected in all the type alloys measured in this project. Antimonial lead is a term used to describe lead alloys containing antimony in proportions of up to 25%. Antimony is added to increase hardness and minimise shrinkage; it permits sharp definition, and reduces the melting point of the alloy compared to pure lead but only if the addition of antimony does not exceed 20 wt% (Fig. 2.4).

Antimony, a silvery white substance, is classified as a non-metal or metalloid, although it has metallic properties in the trivalent state. The material is very brittle and a poor conductor of electricity and heat. It has a melting pint of 630.6°C and a density of 6.7 g/cm^3. It has been traced back as early as 3100 BC in the form of Antimony (III) sulphide (Sb_2S_3), called Stibnite (Stibium, Sb). In ancient Egypt, it was used as an eye cosmetic (Feneau, 2002).

The first detailed description of a procedure for isolating antimony is to be found in 'De la pirotechnia' (Biringuccio, 1540). It is also described by Agricola in 'De re metallica' although it remains unclear if the metallic form was obtained (Agricola, 1530).

The eutectic temperature of 251.2°C, at 11.2 wt% Sb, shows that 3.5% Sb is soluble in lead (Fig. 2.4). At room temperature, only 0.44% Sb is soluble in lead, and after cooling at a rate lower than that of air cooling, small rods of antimony precipitate from solid solution. After furnace cooling, the rods appear at the grain boundaries; after even slower cooling, they also appear within the grains. After air cooling, the antimony is often retained in solution, permitting subsequent age hardening. The eutectic

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[8] (American Society for Metals, 1990), Binary Alloy Phase Diagrams section

mixture has a lamellar form with particles of antimony in a matrix of lead-rich solid solution. In hypoeutectic alloys (below 11.2% Sb), the lead-rich phase of the eutectic blends into the primary lead-rich phase that is also present, giving the eutectic a divorced appearance. Hypereutectic alloys show angular primary crystals of antimony in the eutectic (American Society for Metals, 1990). The crystal boundary in lead alloys with low antimony contents, such as Pb with 3.5 wt% Sb, has a high concentration of antimony and is called an antimony-rich inter-crystalline phase (Jiang, Lu, Zhao, Gu, & Zhang, 1990).

Another feature that favours antimony as a beneficial alloy component is the ability to expand on solidification. Many texts report that the addition of antimony resulted in an expansion upon solidification of the type alloy in the matrix, thus leaving the most accurate reproduction possible of the cast letter. It is true that antimony expands upon solidification from the liquid state, as do bismuth and water. In type alloys however, there is not sufficient antimony present to benefit from this effect. At least 75% antimony should be present with the lead or lead-tin to have this effect (Thompson, 1930). These high concentrations are never found in type metals since they would be too brittle. Moreover, the melting point of these alloys (about 600°C) would be too hot to handle and to cast in the copper matrices. In addition, such high temperatures would promote oxidation of the copper matrices leading to a possible loss of letterform accuracy. As a result, type metals with low antimony concentrations do retract, but to a lesser extent than pure lead or lead-tin alloys. An average of 2% is measured and on the level of type dimensions, this shrinkage is negligible. The largest benefit is surely in its very low surface tension and low viscosity. These physical facts assure the caster of accurate reproductions of the letters from the matrices.

2.2.3.3 Lead-antimony-tin alloys

Lead-antimony-tin alloys are the most common for the use of type. From the 16th century until the end of the lead type printing era, similar ternary alloys were applied. Exceptions can be found between 1700 and the 1850s, when tin was left out. The ratios of elements determine whether the casting and result of the letter fulfils its pre-set demands. Different authors in historic works on this topic have analysed this knowledge to unravel the use of metals (and their cost at the time) versus the quality that was needed for good printing.

A word on the intermetallic phase of tin and antimony may serve our study. In the lead alloys where tin and antimony are added as alloy substituents, a pseudo-eutectic phase can be formed. This system has a eutectic temperature of 183°C at a composition of 61.9 wt% Sn and has three peritectic reactions (Osamura, 1985). The polymorphism of SbSn was suggested to be an order-disorder transformation. The solid solubility of antimony in tin is appreciable at elevated temperatures, but decreases rapidly as the temperature drops. Chill-cast alloys with antimony contents up to 8% normally consist of a cored solid solution of antimony in tin. Slow cooling allows some precipitation of SbSn, which is evident as white particles between the tin-rich dendrites (SbSn is an intermetallic phase, which has a fairly wide phase field, extending from 41 to 56% Sb).

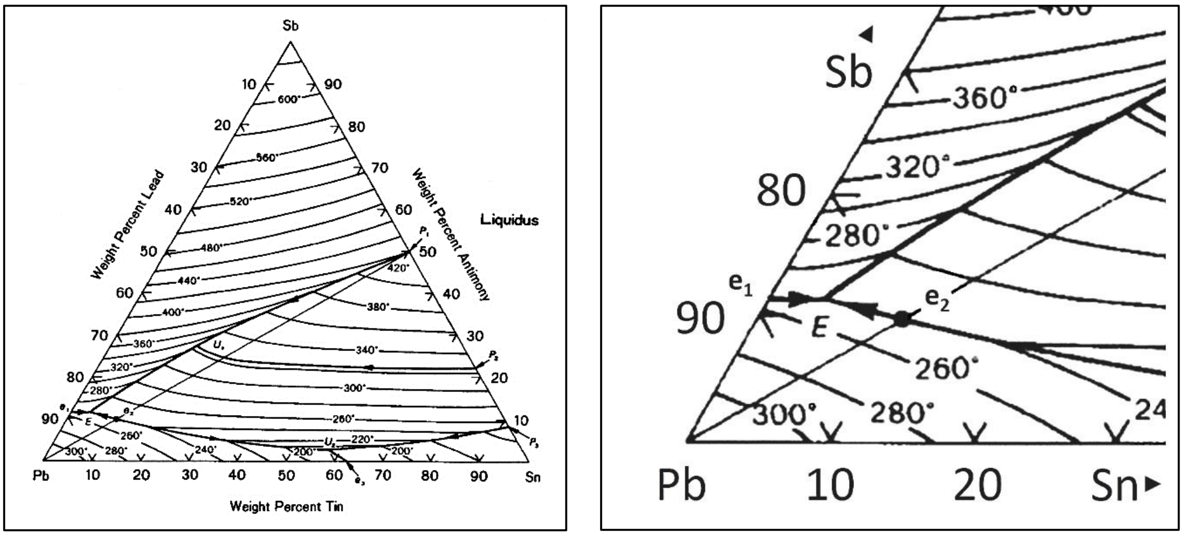

Fig. 2.5: The phase diagram lead-antimony-tin, with on the right a detail of the lead-rich side. Point 'E' indicates the ternary eutectic point at 84/12/4 wt% Pb/Sb/Sn. 'e_1' indicates the Pb-Sb binary eutecticum; 'e_2' indicates the pseudo-eutectic SbSn formation at 10/10 wt% Sb/Sn.[9]

Heat treatment or natural ageing increases the amount of interdendritic SbSn; upon prolonged ageing, an acicular* precipitate of SbSn also appears within the dendrites. At antimony contents exceeding 8%, cuboids of primary SbSn are produced in a tin-rich matrix that is formed by a peritectic reaction between the melt and the primary SbSn. Finely divided particles of SbSn may again precipitate from the tin-rich matrix. At antimony contents of 30 to 40%, primary SbSn precipitates from the melt as irregularly shaped dendrites (American Society for Metals, 1990). The described reactions and formations are very complex when present in a lead rich matrix. It is beyond the scope of this thesis to go into these reactions in the solidification process more in detail. However, historical data and previous analyses on historical types (Part 1.5) show that the majority of lead types compositions lie within the range of lead rich alloys with additions of antimony and tin, near to the eutectic points E, e_1 and e_2 (Fig. 2.5). The choice for binary (Pb-Sb) and ternary alloys (Pb-Sb-Sn) to execute analyses and corrosion tests is therefore based on these alloy compositions. The phases present in the selected alloys will be studied for their compositions and towards corrosion development.

2.2.3.3.1 Melting and casting properties

The primary requirement of an alloy composition is to produce good castings under the conditions of operation. Desirable features are hardness, strength, resistance to compression and wear, but all these are secondary in importance to the 'casting properties' (Thompson, 1930). The reduction of surface tension is a very important for obtaining precise castings. Another beneficial property is a low melting point, which is easier and cheaper to maintain in the melting pot, but also promotes a better flow and slightly slower solidification in the mould. The slow solidification in the mould enables 'the throw', as described in Moxon and Fournier, for accurate reproductions from the matrices. With smaller letters, even if this is only a matter of a fraction of a second, it could just make the difference between a good or a bad casting (Moxon, 1683) (Fournier, 1764).

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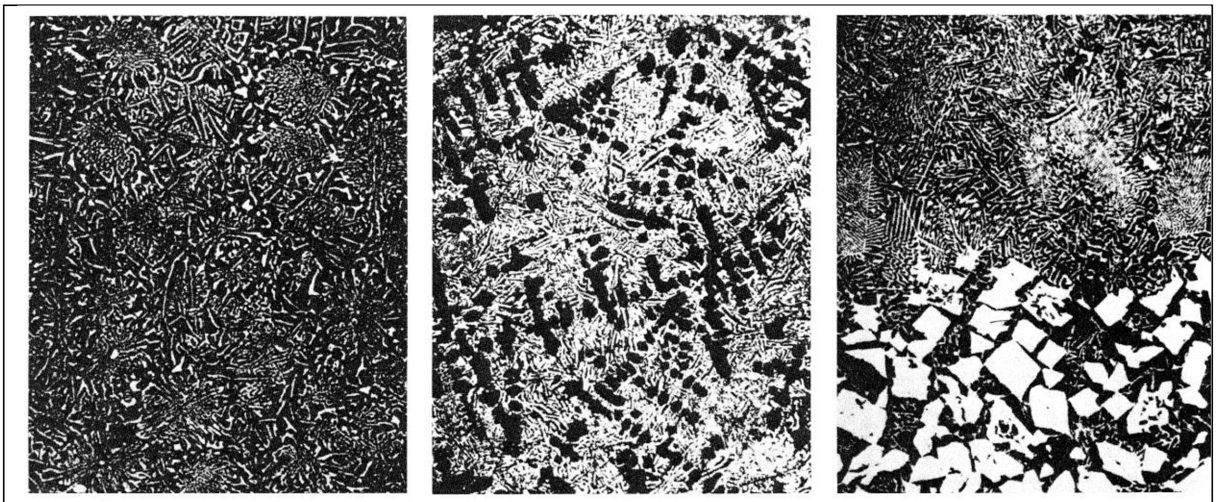
[9] (Osamura, 1985)

Walter Wilkes (Wilkes, 1990) assumes that from the beginning of letter casting, alloys must have consisted of lead, antimony and tin. The right ratios were to be found through empirical experience. In any case, the alloy must meet the following desired specifications: 1) a sharp cast in the mould, without inclusion of air; 2) when cooled down, the dimensions must be exact; 3) it must be easy to cast, indicating a low melting point so that it will not adhere to the iron or other metals of the moulds or machines; 4) it must melt completely, meaning it should give as little as possible resistance while casting, and remelts easily without losses; 5) it must be rigid to withstand handling and printing; 6) the surface must take on ink well and print clearly; 7) it should be physiologically safe; and 8) it should be reasonably priced. The best alloy possible is composed of lead, antimony and tin. Antimony gives the alloy the sharpness and hardness it requires. Tin is rigid and gives the alloy toughness, resistance to wear and makes it easy to flow.

On the physical specifications of lead and antimony, Wilkes explains the drop in melting temperature by adding antimony to the lead, until the eutectic point is reached (see Fig. 2.4) at the point of 88.8 wt% Pb- 11.2 wt% Sb. Adding more antimony increases the melting point again. It is clear that the further the alloy in the phase diagram is from the eutectic point, the longer it will take time to cool down completely to the solid phase, which in all cases is 252°C. This is undesirable for a high working speed, except for small letters which cool down immediately anyway.

The addition of tin does not alter the above-mentioned specifications much. An alloy composed of 84/12/4 wt% Pb/Sb/Sn maintains the same eutectic behaviour but runs more easily. This alloy can also be called the three-metals eutectic, melting at 240°C. Here, the tin-antimony phase cannot be distinguished because of the complete dissolution. The microstructure is very dependent on the exact presence of each metal in the alloy. Different examples are given in Fig. 2.6.



[224] Eutektische Legierung, Gefüge mit feiner Struktur

[225] Mehr Blei als das Eutektikum; es scheidet sich in (dunklen) Kristallen ab

[226] Zinn-Antimon-Mischkristalle haben sich würfelförmig zur Oberfläche hin abgelagert

Fig. 2.6: Metallographic images[10] showing from left to right a eutectic alloy with a very finely dispersed microstructure; a hypoeutectic alloy where the abundant lead is shown as dark crystals and finally tin-antimony cubic crystals near the surface of the cast alloy piece.

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[10] (Wilkes, 1990)

Investigations at the beginning of the 20th century (Dean, 1923) were conducted by thermal analysis. At that time, the compound SbSn was not distinguishable microscopically from the Sb primary solid solution. In the 1930s, the ternary phase diagram progressed remarkably with the definition of true ternary eutectic point. The values for this are accepted as 240°C and 12 wt% Sb and 4 wt% Sn. In 1935 this was confirmed and added as a pseudo binary eutectic at a value of 245°C. The eutectic composition is consistently given as 80 wt% Pb, 10 wt% Sb and 10 wt% Sn .

Osamura (Osamura, 1985) also dedicates the Pb-Sb-Sn alloys to the earlier printing industry, designating them as 'type metals', containing 10 to 24 wt% Sb and 2 to 12 wt% Sn. These alloys are also used as bearing metals known as Pb-base 'white metals', containing 10 to 20 wt% Sb and 5 to 10 wt% Sn, with less than 0.5 wt% Cu.

One of the two peritectics in the antimony-tin system occurs at 425°C (797°F), where molten metal reacts with antimony-rich solid solution to form SbSn. Both antimony and tin are moderately soluble in SbSn, resulting in a phase field extending at room temperature from approximately 44 to 59% Sn. At approximately 10% Sb, 10% Sn, and 247°C (476°F), the Pb-SbSn pseudo binary system contains a eutectic that has a lamellar form, with particles of SbSn-rich phase in a matrix of lead-rich solid solution. The eutectic point lies in the liquidus surface of the ternary diagram. The form of the ternary eutectic mixture is also lamellar, with particles of both SbSn-rich phase and antimony-rich solid solution in a matrix of lead-rich solid solution.

The formation of solid phases (crystals) in a casting process depends on the rate of solidification and is also related to the method of casting. Historical casting processes were always 'gravity casting' as opposed to later and more technical advanced casting processes such as centrifugal, vacuum or pressure casting. Examples of different structures in the same alloy after a gravity cast or a centrifugal cast are shown in Fig. 2.7. A gravity cast shows more abundant SbSn crystals whereas a centrifugal cast has many large distinct cubic SbSn inclusions. It is however not specified whether this is due to the casting action itself, the melting temperature, or the cooling rate in the mould.

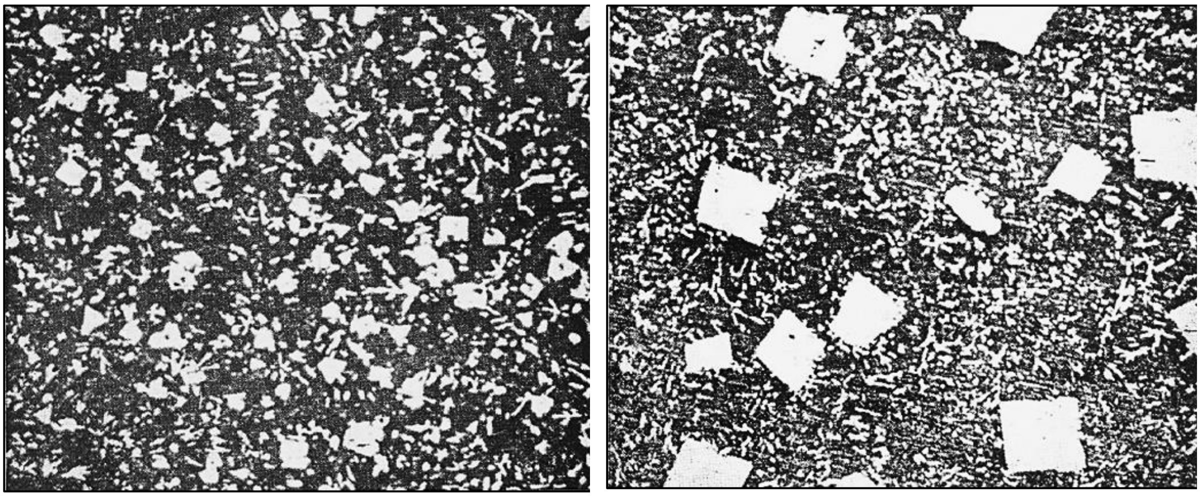

Fig. 2.7: Left: A gravity cast of a tin-base white metal containing antimony and copper (etched Nital); Right: Centrifugally cast of the same alloy.[11]

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[11] (Wilkes, 1990)

2.2.3.3.2 Mechanical stress and creep

Type alloys have to withstand different kinds of mechanical stress. First, there is the finishing of each type piece after casting, which includes the break-off of the ingot piece and the filing or shaving to the correct height. Secondly, the manipulation to collect them in the letter cases, the taking out by the composer to form the lines, the arrangement in the holder and finally their position in the standing type page. Thirdly, the printing itself, when the screw press pushes the paper onto the standing type to transfer the ink from the types to the wetted paper, hundreds or thousands of times. Finally, for a new distribution of the types they had to be removed from the composition, cleaned and put (thrown) again into the correct compartments of the letter cases.

It is quite easy to assume that harder alloys will be able to withstand all of the above-mentioned manipulations for longer. For that purpose, antimony was usually added to the lead, whereas tin mostly served as an element to make the cast metal more fluid. Besides the intrinsic hardness values of the different type alloys employed, creep could also play a role in the good preservation of the types. Creep is the result of a relatively low force applied over a longer period of time. Even at room temperature, deformations can occur in solid metals or alloys, when they are put under these kinds of stress. Lead and tin are subject to creep, but also a number of lead-based alloys with antimony seem to develop plastic deformations due to creep.

Lead, lead-copper (0.06 wt% Cu) and lead-antimony (1.2 wt% Sb) alloys were compared with variable loads (1 - 12.5 N/mm^2) over a long period of time (up to 50 days) and at different temperatures (5 – 60°C). The results show that the addition of copper or antimony leads to less susceptibility to primary creep compared to pure lead. However, secondary creep is higher with elevated loads and temperatures for each of the alloys compared to pure lead (Sahota & Riddington, 2000).

Tin and tin-antimony alloys were studied for use as lead-free solders. Creep deformation tests were applied to pure tin and a tin-based alloy with 5 wt% antimony with various stresses (1–30 MPa), activation energies (44.7–60.3 kJ/mol) and temperatures (296–473 K). While antimony reduces the creep as compared to pure tin, it still shows an increase in strain rates versus the normalised stress.

Impression creep behaviour of cast Pb-Sb alloys (resp. 1.25 and 4.5 wt% Sb)[12] is described to be a grain boundary diffusion process at low stress induction, while a dislocation creep mechanism is shown at high stress regimes (Mahmudi & Rezaee-Bazzaz, 2005). Impression creep occurs more readily in the alloy with a lesser Sb content.

2.2.3.3.3 Age-hardening

The mechanical properties of many low melting alloys change gradually with time at room temperature because of minute changes in structure. This ageing at room temperature is sometimes referred to as room temperature recrystallisation or annealing. Ageing sometimes has the effect of increasing the hardness and strength of the alloy, but it can also have the opposite effect (Lampe, 1976). These phenomena could play a role in the ageing of the historical types in the museum's collection. However, the many manipulations of the types through the time of use, the variation in atmospheric conditions

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[12] Note: It is unclear if atomic percent (at%) or weight percent (wt%) was used for these numbers.

while in storage or on exhibition, the many variations in alloy compositions and the presence of corrosion make it very complex to study. It is beyond the scope of this study to go into this matter.

2.2.3.4 Iron

In type metal, iron may be present. Its origin is mostly related to the presence of antimony, because iron nails were used in the reduction process from stibnite to metallic antimony (Moxon, 1683). The presence of iron can also be due to wearing of the ladle or melting pot. There only seem to be traces in the measured contents of historic type. Since no binary phase diagrams are available, the melting temperatures of both metals differ greatly (Pb: 327.5°C, Fe: 1,538°C) and iron is lighter compared to lead (Fe density 7.9 g/cm^3, Pb 11.3 g/cm^3), it is expected that the iron is not dissolved in the lead and floats in the melting pot to the surface where it oxidises and is removed.

2.2.3.5 Copper

Copper is often found in type metal and was probably added deliberately to strengthen the alloy. This was also common practice, even before the days of printing, with tin tableware to make it less vulnerable to bumps and dents. In the 15th century, the Worshipful Company of Pewterers controlled the grades of pewter, where the so-called ‘fine metal’ consisted of tin with as much copper as it could absorb, which is about 1% (Dwenger, 1965). The measured contents in type metal do not normally exceed 0.5 wt%. The solubility in lead is 0.005 % at room temperature (Costa, 2005).

2.2.3.6 Silver

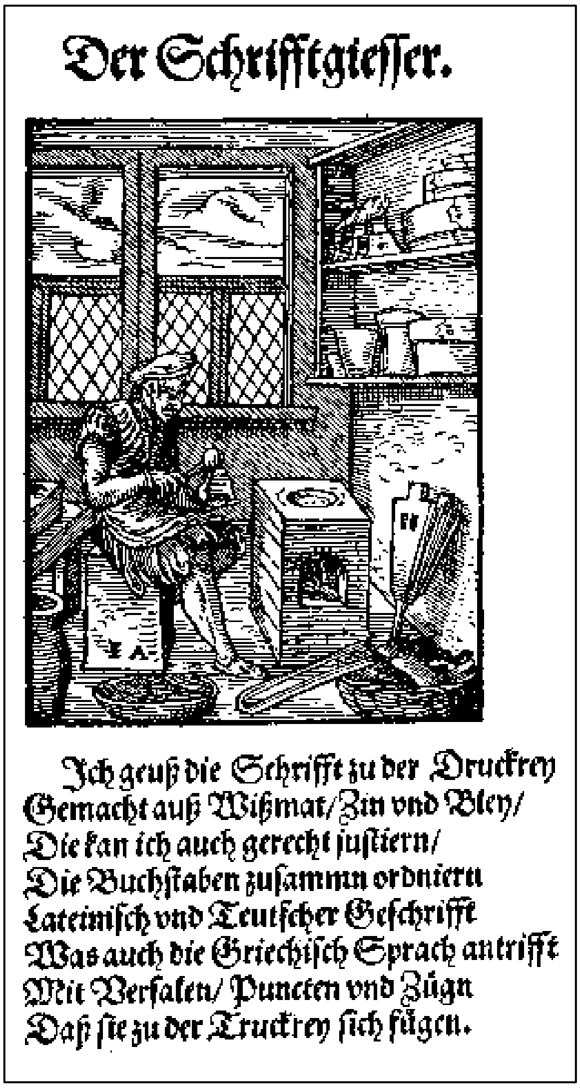
Silver is of particular interest in the casting of type, not so much as a genuine alloying element but rather as part of an elaborate myth that has developed through the centuries and is still believed by some to be true. The first mention of type being cast in or with silver comes from Paulus Pater, who states in 1710 on account of its wonderful smallness and clearness, that the Dutch Nonpareil letter was called by many the ‘silver letter’, because it was assumed to have been cast in that metal. Other sources which are mentioned on this matter are described in a footnote by Reed (p. 101): ‘*L. Giucciardini in the Descrittione di tutti I paesi bassi, 1587, that Aldus Manutius was said to have used them; Hulsemann describes that Robert Estienne’s Bible in 1557 was printed with ‘typis argenteis sane elegantissimis’* (Reed, 1952). Why anyone would use silver for printing letters is not clear, at least not from a technical point of view. Cunradi (1785) still mentions the use of silver by the Dutch printers’ family Elsevier: *'Die Holländischen Druckereien hatten ehedem Lettern aus Silber, z.B. die Elzevirischen Edizionen sind Silberdruck*‘, translated to mean that ‘Dutch printers have silver letters, for example the Elsevier editions are silver printed‘ (Cunradi, 1785).

Silver does not add any significant chemical or physical advantage to a tin- or lead-based alloy. As an alloying element, its presence is not of any more importance than tin in lead or lead in tin; it may change the hardness very slightly, and it may increase the corrosion resistance, but from a metallographic point of view, considering the very high cost of this metal, it makes no sense to add silver to the alloy. As a conclusion, the bright and shiny appearance especially on small letters must find its origin in the use of a higher amount of tin. Higher amounts of tin were used in lead alloys to enhance the fluidity of the lead alloy, which was needed for the smallest type to be cast flawlessly. The solubility of silver in lead is about 0.02 % at room temperature (Costa, 2005).

2.2.3.7 Bismuth

Bismuth as an alloying element in type metal has long been a point of discussion. Until recently, the most common source for the assumption that bismuth was actually used in type metal came from the illustration by Jost Amman (1568) and the accompanying text, mentioning ‘Wizmat, Zin und Bley’. (Fig. 2.8)

However, recent measurements on 16th-17th centuries types from Wittemberg lead to the conclusion that bismuth would have been added deliberately to the melt for type metal (Berger & Stieme, 2014). No direct advantage in adding Bismuth can be seen. Bismuth does expand on solidification, but as for antimony, the content in the alloy is too low to benefit from this. It is possible that it diminishes the shrinkage of the lead somewhat. It is also possible that it was just at hand and could be added cheaply and harmlessly to the melt, although all of this is hypothetical.



Der Schrifftgieſſer.

Ich geuß die Schrifft zu der Druckrey
Gemacht auß Wißmat/Zin vnd Bley/
Die kan ich auch gerecht juſtiern/
Die Buchſtaben zuſammn ordniern
Lateiniſch vnd Teutſcher Geſchrifft
Was auch die Griechiſch Sprach antrifft
Mit Verſalen/ Puncten vnd Zügn
Daß ſie zu der Truckrey ſich fügen.

Fig. 2.8: Woodcut by Jost Amman, ‘Beschreibung aller Stände’, 1568: 2nd line mentions that the type metal is made with ‘*Wizmat/ Zin und Bley*’, being probably ‘Bismuth, Tin and Lead’.

2.2.3.8 Mercury

Mercury is a bright, silvery white metal with the symbol Hg, retrieved from the Greek name hydrargyrum, meaning ‘liquid silver’. The metal is liquid at room temperature and becomes solid at a temperature of -38.8°C (Feneau, 2002). It is a poor conductor of heat, but a fair conductor of electricity. Mercury can form an amalgam, already at room temperature, in combination with most metals, except for iron, nickel and platinum. Gold, silver, copper, lead and tin diffuse easily with mercury. It is not expected that mercury was added to the alloy as a constituting element, but it may be possible that mercury dissolved into used type metal by the reduction from the vermilion (mercury sulphide) based red ink that was used. If so, it could lead to very particular corrosion processes and possible problems for the conservation of these pieces (De Ryck, Adriaens, Storme, & Adams, 2004). At this moment, however, there is no evidence for this assumption.

2.2.4 Copper

Copper was the main metal used to produce the matrices, or more precisely the strikes from the punches. Although the purest copper was recommended by historic authors such as Biringuccio, Moxon and Fournier, the refining methods of Renaissance times were not able to remove all traces of other metals from the ore or the smelting processes.

Like gold, copper is one of the few metals to have a clear specific colour: salmon pink. It often appears redder because of the oxidation process. Upon exposure to the atmosphere, green, blue or brown corrosion products can evolve. Copper is fairly ductile, but harder than lead, tin, gold or silver, and has a melting point of 1084°C.

The most common copper alloys are bronze (addition of tin) and brass (addition of zinc). Bronzes mostly contain between 5 and 20% tin (Fig. 2.9), but in many cases also contain zinc and/or lead for cast objects. Brasses can consist of up to 35 % zinc, maintaining their highly plastic deformation capacities because of the α-solid solution* (Fig. 2.10, indicated (Cu)). Zinc contents below 1-2 % are considered to be non-intentional additions to the copper. Brasses with zinc concentrations up to 15 % are so-called ‘red brass’ or ‘tombak’. Higher zinc values have a more distinctive golden-yellow colour. In Europe, the first use of brass was only possible with the smelting of copper-zinc ores, giving a brass alloy in the process. Zinc has the specific property of evaporating below the roasting* temperature of about 1000°C. After importing metallic zinc from the Orient in the 16th and 17th centuries, it was also possible in Europe to obtain metallic zinc from its ores by cooling down the zinc fumes.

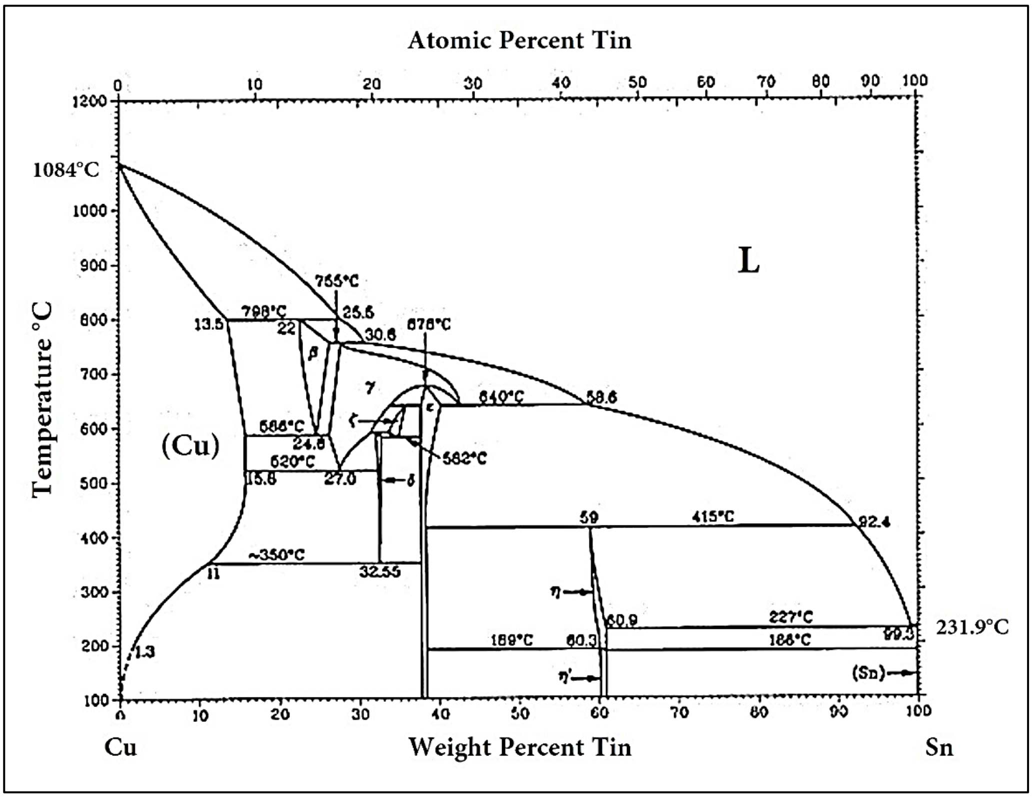


Fig. 2.9: Binary phase diagram of bronze (copper with tin).[13]

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[13] (American Society for Metals, 1990), Binary Alloy Phase Diagrams Section

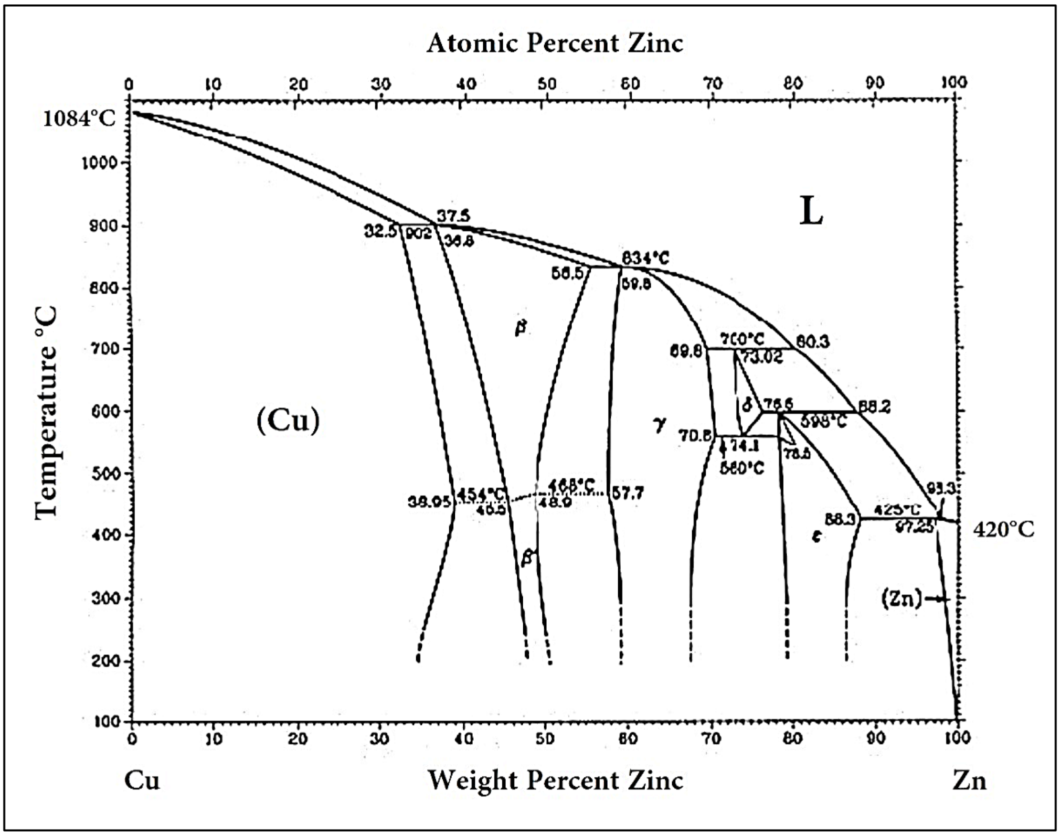

Fig. 2.10: Binary phase diagram of brass (copper with zinc).[14]

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[14] (American Society for Metals, 1990), Binary Alloy Phase Diagrams section

2.3 Corrosion

2.3.1 Introduction

Some museum collections include lead alloyed objects, which, under specific atmospheric conditions, develop severe corrosion. This corrosion deforms the object, diminishes readability, causes loss of historical information and may lead to the complete destruction of the object itself (Costa, 2005). It was noticed that some lead alloys were more prone to corrosion than others, as was seen in the Plantin-Moretus Museum. The vast collection of historic printing letters (type) is endangered and was studied in previous years to determine the causes of this corrosion development. The atmospheric conditions were monitored (Krupińska, van Grieken, & De Wael, 2013), and the elemental composition of the type alloys were studied (Storme, Jacobs, & Lieten, 2013).

Lead is very susceptible to corrosion in acidic environments. In this respect, many historical museum settings or wooden showcases are not favourable environments. Similar corrosion processes can be observed with church organs, where the lead pipes also suffer from corrosion, due to the evaporation of volatile acids from the oak parts of the instrument (Chiavari, et al., 2008). However, it is known that tin inhibits the corrosion of lead when alloyed with at least 2 w%. Recent research has shown that the presence of antimony greatly exacerbates the corrosion of lead (Ghiara, et al., 2014). This was also recorded from the analyses on the heavily corroded type objects from the Plantin-Moretus Museum collection. There it became clear that type with high levels of antimony and no (or very low amounts) of tin were prone to a severe corrosion process (Storme, Jacobs, & Lieten, 2013). It may be reassuring that only a minority of the collection has suffered from this condition; nonetheless, it is an important issue that needs to be addressed. No conservation technique can recover a type's face when it has been corroded. Only type with a thin oxidation layer, still with intact shapes of the letter, can be kept in this condition. To do so, appropriate preventive measurements and/or conservation techniques for superficial cleaning, such as electrochemical processes, can be applied (Degrigny & Le Gall, 1999). To safeguard the metal from new corrosion, protective layers or dedicated storage packing and acclimatisation can be used (Chiavari, Martini, Poli, & Prandstraller, 2004). In any case, understanding the alloy composition and its corrosion reactions in the atmosphere where the object is kept, is vital for optimal conservation.

2.3.2 Lead

Lead objects exposed to atmospheric or burial conditions usually corrode only slightly since the formation of a protective film, mainly constituting lead carbonates, inhibits corrosion (Graedel, 1994). In a non-polluted indoor environment, monoxides (natural oxide layer) like litharge and massicot are formed on the surface. These oxides can react with moisture and carbon dioxide gases and form stable, insoluble corrosion products on the surface. This layer may consist of stable lead sulphate as anglesite ($PbSO_4$) (Costa, 2005), platternite (PbO_2) (Green, 1989), lead carbonate or cerussite ($PbCO_3$), basic lead carbonate or hydrocerussite ($Pb_3(CO_3)_2(OH)_2$) or plumbonacrite ($Pb_{10}(CO_3)_6O(OH)_6$) (Rocca & Steinmetz, 2001). It is possible that the protective layer may be absent. In that case, lead will be constantly attacked by various elements in the environment. Lead salts will then be converted into basic lead carbonates, which is a stable form by itself. But the presence of weak acids, organic acids, lipids and oils can penetrate this protective layer (Stambolov, 1994) (Turgoose, 1985).

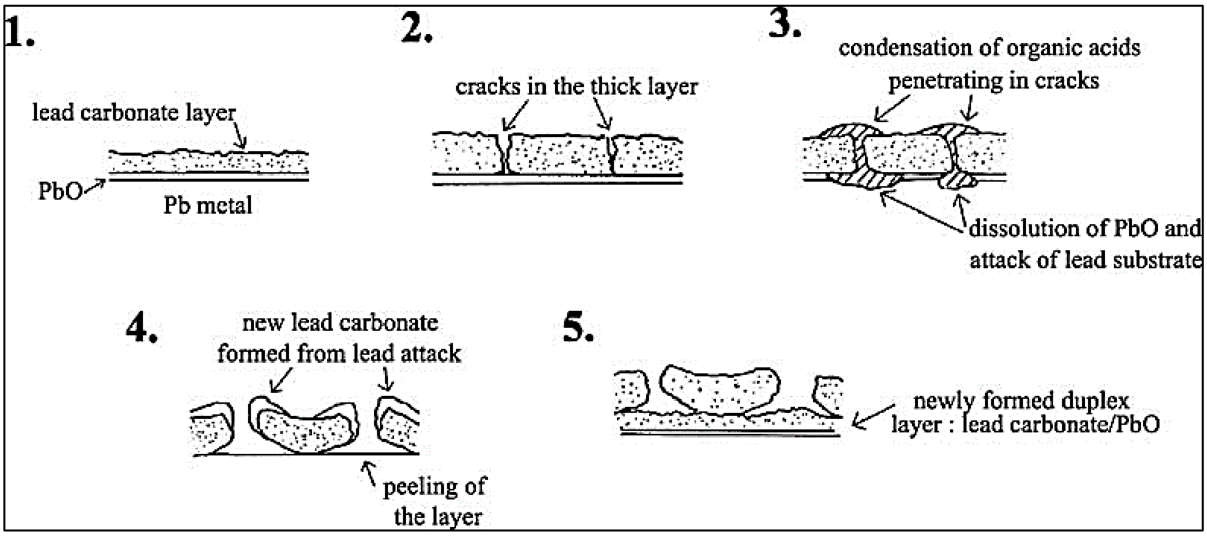

Fig. 2.11: Schematic mechanism of lead corrosion by organic acids leading to multiple layers of lead carbonate compounds.[15]

The high reactivity of Pb alloys to volatile organic acids (VOC's) has been widely recognised in studies of church organs (Chiavari, Martini, Poli, & Prandstraller, 2004) (Chiavari, et al., 2008). Organic acids and formaldehyde catalyse lead corrosion, in the presence of humidity, oxygen and carbon dioxide (Enderly & Lane, 1985). The corrosion of lead by formaldehyde only seems to occur at 100% relative humidity and not at 50% (Raychaudhuri & Bumblecombe, 2000).Lead in combination with organic acid vapours will lose its protective layer, and oxidation of lead will occur. Soluble salts will be formed, like lead acetate and lead formate (Selwyn, 2004). The vapours of the organic acids are condensed in an aqueous layer upon the lead surface. The compounds (for example, lead carbonates) in the passive layer dissolve into soluble compounds (such as lead acetate). This solution (of acetate compounds) migrates and penetrates into the cracks in the ancient corrosion layer towards the metal surface (Fig. 2.11). The acetate solution dissolves the lead oxide (PbO), causing the peeling of the lead carbonate layer. New carbonate compounds are formed on top of the lead carbonate layer, by the release of Pb^{2+} cations. Once the full carbonate layer is dissolved, the metal can corrode again (Rocca, Rapin, & Mirambet, 2004). This corrosion can continue, as a continuous or cyclical process, until no metal core remains. These effects of cracked, non-adherent and non-protective corrosion layers were also found on corroded organ pipes (Speerstra, J., 2011).

Formic acid attacks lead, forming lead formate ($Pb(HCO_2)_3$), reflected in straight threads on the surface (Selwyn, 2004). An amount of 0.04 ppm formic acid makes the lead surface dark, while more than 0.1 ppm causes an increase in weight (Tétreault, et al., 2003). Acetic acid forms a thick, loose, white layer on the lead surface (which starts already at 1 ppm acetic acid) (Selwyn, 2004), unlike formic acid, which forms thin dark layers.

Lead is resistant to sulphuric acid because of the formation of stable sulphate corrosion products but is susceptible to nitric, hydrochloric, and especially carboxylic acids, specifically with high humidity levels and in the presence of organic acids (Tétreault, Sirois, & Stamatopoulou, 1998) (Graedel, 1994).

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[15] (Rocca, Rapin, & Mirambet, 2004), p. 654.

For historic objects, it is often found in practice that 19th century items are much more prone to corrosion than older objects. This is seen in lead cames from stained-glass windows[16] and also on inlayed Japanese lacquered objects (Heath & Martin, 1988). It is unclear exactly what is responsible for this occurrence, but most probably it has to do with minor alloying elements which inhibit corrosion reactions.

2.3.3 Lead alloys

Besides the primary influence of the environment, the different alloy materials also have an influence on the corrosion formation. The chemical properties, distribution and phases of the alloyed metals play a major role, but also the presence of impurities and all possible actions to which the metal has been subjected (De Ryck, et al., 2004) (Schotte & Adriaens, 2006). Concerning structural features, it has been demonstrated that traces of foreign elements are sufficient to promote different phases; their distribution in the matrix has decisive consequences for the properties and conservation of lead objects (Costa, 2005). The melting temperature, the presence of oxides in the melt, the distribution of elements in the melting process, the cooling rate on casting, etc., all have a significant influence on the grain size and phase formation of each distinct alloy.

2.3.3.1 Lead-tin corrosion

Like lead, tin also occurs frequently in the alloys of the printing letters. Tin is very stable under normal atmospheric conditions. In a dry environment, the formation of corrosion on tin is very slow, but when it is exposed to moisture and oxygen, it loses its lustre, becoming granular and grey in appearance.

This grey stannous oxidation layer (tin (IV) oxide, SnO_2), the most common and stable corrosion form of tin, can be converted to a higher form of oxidation, namely the stannic oxide (SnO), which is nearly white in colour. This latter occurs mostly as a secondary reaction in the presence of soluble salts (Plenderleith, 1957) (Ankersmit, 2008). In the presence of humidity and contaminating gases the percentage of oxidation increases and the surface of the metal takes on a yellowish colour (Degrigny, 2000) (Stambolov., 1985). Tin objects that are kept in museums can show several corrosion compounds such as cassiterite (SnO_2), romarchite (SnO) and hydroromarchite ($5SnO \cdot 2H_2O$) (Bannister, 1926).

Tin pest occurs relatively fast in its formation and is catastrophic in its result. This type of corrosion rarely occurs in museums, and only in exceptional circumstances. The α-phase has a density of only $5.77 g/cm^3$; it is very brittle and has little strength. The transformation from the β-phase to the α-phase takes place in theory below 13°C, but in reality the temperature needs to be constantly far below 0°C. When this transformation occurs, the metal expands and disintegrates into a coarse, friable grey powder. This 'tin pest' phenomenon is prevented as soon as a small amount of antimony or lead (0,1 wt% Pb) is present in the alloy (Selwyn, 2004).

In lead-tin alloy objects, lead is less abundant in the corrosion than in the bulk material. This is because the lead corrosion may be more soluble than tin corrosion products on which they might migrate away from the surface (Turgoose, 1985). Moreover, the colour of old pewter changes over time compared to modern pewter, because of the presence of lead in the alloy. The more lead in a lead-tin alloy, the

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[16] Oral information Prof. dr. J. Caen, 2016

more sensitive the metal is to corrosion. In other words, tin offers more resistance to corrosion in a lead alloy (Selwyn, 2004) (Costa, 2005) (Speerstra, J., 2011). At very high relative humidity levels, the addition of up to 9.7 wt% Sn is only slightly beneficial; however, at RH levels of 60 %, the addition of as little as 0.56 wt% only causes a corrosion process with a mass gain of 50 % compared to pure lead (Speerstra, J., 2011).

2.3.3.2 Lead-antimony corrosion

Antimony is detected in all the letter alloys measured in this project. It is a relatively stable material and is not easily influenced by air or moisture, although in controlled conditions antimony can react with oxygen and form several oxides: Sb_2O_3, Sb_2O_4 and Sb_2O_5 (Wang, 1919). In anaerobic conditions on the other hand, antimony is stable and does not dissolve over a wide pH range. Antimony forms complex ions with organic acids. Certain conditions of pH, oxidation potential and temperature promote the corrosion or dissolution of antimony in aqueous systems.

The influence of antimony in a lead alloy, at high concentrations (10-16% Sb), has been mentioned before (Degrigny & Le Gall, 1999), but only recently addressed in more detail (Storme, Jacobs, & Lieten, 2013) (Ghiara, et al., 2014). It is shown that the presence of antimony in lead greatly promotes corrosion to VOC's. The corrosion development of a range of lead-antimony binary alloys is addressed in chapter 6.

2.3.3.3 Lead-antimony-tin corrosion

The corrosion of these ternary alloys is mostly related to historic printing letters. Whereas initial observations have been made on the type collection of the Museum Plantin-Moretus in Antwerp (Storme, Jacobs, & Lieten, 2013), followed by Raman investigations on mock-ups (Ghiara, et al., 2014) and a comparison of composition and corrosion developments between type from the Antwerp collection and the archaeological finds from Kralice, Czech Republic, further investigations are needed to fully understand the corrosion development of these alloys.

Analyses have shown that lead alloys with high amounts of Sb and low amounts or absence of Sn, undergo fierce corrosion in acid environments, especially with the presence of formic acids. µ-Raman studies on lead samples show the presence of lead formates (besides cerussite, hydrocerussite and metallic antimony) from oak, beech and hardboard from test series in an Oddy test* (Martini, 2012). In 2014, a series of XRD measurements in reflection at the Chemistry Department of the University of Antwerp (Research group AXES)[17] also confirm cerussite, hydrocerussite, lead formate, metallic Pb and Sb (see Chapter 6, XRD results). A preliminary conclusion would be that cerussite and hydrocerussite are developed first (detected at the bulk-corrosion interface) and afterwards, on forming a thicker corrosion crust, lead formates develop. Earlier XRD measurements (powder diffraction)[18] have indicated the presence of lead acetate hydrates, while cerussite, hydrocerussite, metallic lead and antimony are shown too. XRD measurements with an XRF/XRD surface monitor at the UGent[19] again show cerussite and hydrocerussite (although it is often difficult to distinguish between them) and lead

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[17] Executed by Vanmeert and Janssens, 2014, report to the author.
[18] Executed by Abakunov and Grieten, 2012, report to the author.
[19] Executed by Van De Voorde and Vekemans, 2014, report to the author.

formates. Possible antimony oxides are present as well, but due to the overlap of the most intense matched peaks of cerussite and lead formates, this is not conclusive.

Overall, it can be concluded that if tin is also present in the lead-antimony alloy, corrosion is inhibited. However, it is still unclear what concentrations of tin versus antimony determine the corrosion development in particular atmospheric conditions. This is being looked at in chapter 6.

2.3.3.4 Copper

Copper in type alloys often occurs with the presence of tin. Only low concentrations (max. 0.5 wt%) were measured, and influences on the corrosion behaviour of Pb-Sb-Sn alloys are not known. In lead as in tin alloys, however, copper can accelerate corrosion (Speerstra, J., 2011) (De Ryck, et al., 2004).

2.3.3.5 Silver

Silver is sometimes present in type alloys, albeit in very low concentrations. Silver would inhibit lead corrosion to some extent (Mao & Rao, 1971). Silver in very low concentrations is soluble in the lead rich matrix, with a maximum of 99.81 wt% at 304°C. Solubility decreases with slow cooling down to room temperature, but if cast alloys are considered, a rapid cooling will freeze the silver content in the lead rich grains when the concentration is less than 0.19 wt%.

2.3.3.6 Iron

Traces have been measured in type alloys, but it is not known whether the presence is of any significance in terms of corrosion development. Considering the high melting point of iron (about 1538°C), precipitation at the grain boundaries of the lead rich phases is to be expected. If so, it could lead to localised corrosion phenomena comparable to Cu or Sb.

2.3.3.7 Bismuth

Lead-antimony-bismuth alloys seem to occur in historic German type (Berger & Stieme, 2014). However, it is not known how the presence of bismuth in a lead-antimony (-tin) alloy influences the corrosion rate.

2.3.3.8 Mercury (Amalgam) corrosion

Mercury can be present from the use of red inks, which were made with cinnabar (vermillion, HgS) as a colorant. Mercury does not react with most acids, although it dissolves in hot sulphuric acid and concentrated nitric acid (Feneau, 2002).

The corrosion of an amalgam was also investigated, regarding tin mercury mirrors (Hadsund, 1993). The corrosion manifests in small, dark spots, white (cassiterite), black (romarchite) and yellow-brown (cassiterite and romarchite) corrosion products. The corrosion starts at the edges of the mirror. No mercury was detected in the corrosion, because mercury evaporates or excretes. This corresponds with the formation of tin oxides occurring with tin inlay decorations in wooden cabinets (De Ryck, Adriaens, Storme, & Adams, 2004).

Galvanic corrosion can occur in an amalgam since mercury (0.798 V/SHE) is more noble than tin (-0.14 V/SHE) and thus accelerates corrosion in the tin rich phase, in the presence of moisture. Consequently, mercury in the corrosion layer can attract chlorides and tin will oxidise, so liquid mercury will be released in the alloy. Tin amalgams can suffer from galvanic corrosion, where the mercury-rich liquid phase accelerates the corrosion of the tin-rich solid phase. When the tin corrodes, it forms tin oxides and releases more liquid mercury to the mixture, which perpetuates the corrosion (Selwyn, 2004). It is unclear whether mercury from vermillion in red ink plays a role in the deterioration of type.

2.4 The museum environment

The environmental conditions in the historical museum are not favourable for lead-based alloys. Antwerp and its port in the proximity of the city centre are involved in large-scale industrial activities, contributing to Flanders being one of Europe’s most polluted areas. Although emissions of SO_2, NOx and CO_2 have been falling over the last decade (Milieumaatschappij, 2015), it cannot be denied that these pollutants may have contributed to the air aggressiveness in general and to the museum environments specifically. It is also known that acidic atmospheres promote lead corrosion. Because of the abundance of oak in the building’s floors, beams, and windows but also the furniture, presses, trays, etc., high levels of acids were measured (Krupińska, van Grieken, & De Wael, 2013). In addition to the occurrence of acidic gasses in the indoor environment, a relative humidity level (RH) of about 55% is aimed at, for the preservation of the building and all of its interior wooden artefacts. For metal conservation however, this RH is rather high and promotes ion exchanges between the metal and its surroundings, resulting in corrosion.

The role of organic acids in the corrosion of lead objects such as organ pipes or decorative inlayed lacquered objects has been widely studied (Chiavari, Martini, Poli, & Prandstraller, 2004) (Niklasson, Johansson, & Svensson, 2004) (Heath & Martin, 1988). There is evidence that chemical changes on the metal surfaces vary substantially in different environments throughout time.

The two most influential factors are volatile organic compounds of the museum air, due to the abundance of oak on the one hand, and the presence of high antimony levels in the lead type on the other. The corrosive effect of this combination is known (Degrigny & Le Gall, 1999), but it was noticed that the presence of tin in the lead-antimony alloys plays an important inhibiting role. The scarce literature on ternary Pb-Sb-Sn alloys does not provide specific information on the elemental ratios, related to specific atmospheric corrosive conditions. Moreover, these alloys have complex phases with a ternary eutectic point, a binary pseudo-eutectic point and three main phases, which have a large variation in microstructures (Osamura, 1985). Since the type was originally cast by hand in the print shop (Moxon, 1683), there is little consistency in the alloy composition or homogeneity. The working conditions (Fournier, 1764) and the absence of alloy analyses at the time has led to inconsistent results for the cast type pieces.

Different kinds of wood, varnishes and paints are frequently used in museums. Lead objects are often stored in small, sealed, wooden cabinets or displays (Rocca, Rapin, & Mirambet, 2004). These materials emit organic acids or carboxylic acids. These acids– acetic-, formic-, propanoic- and tannic – are the result of hydrolysis of the acetyl groups of the hemicellulose in wood. Softwood emits fewer organic acids than hardwood, because softwood has a smaller concentration of acetyl groups (Table 2.1). Hardwood, like oak, emits the highest concentration of acetic acid, which is considered the most corrosive of the organic acids (Gibson & Watt, 2010). When manufactured timbers like triplex or multiplex (plywood) are used, vapours (for example, formaldehyde) are released from the glue (Degrigny & Le Gall, 1999). Furthermore, the temperature has a major impact on the amount of corrosion, where a higher temperature leads to a higher corrosion rate. The same applies to relative humidity: the higher the relative humidity, the higher the corrosion rate. The lower the humidity, the less acetyl hydrolysis occurs (Gibson & Watt, 2010).

Table 2.1: Sources and typical ranges of organic acids.[20]

Organic acids	Sources	Typical range levels (ppmv)
Acetic acid	Rooms	0.02 - 0.04
	Outdoor: clean to polluted sites	0.01 – 0.1
	Wooden enclosures (new and old)	0.03 - 1
	Oak (old)	0.1 - 3
Formic acid	Outdoor: clean to polluted sites	0.00005 - 0.01
	Rooms	0.00005 - 0.02
	Wooden enclosures (new and old)	0.01 1
Formaldehyde	Outdoor: clean to polluted sites	0.004 - 0.02
	Rooms	0.008 - 0.06
	Wooden enclosures (new and old)	0.04 - 0.4

The values of acids inside the Museum Plantin-Moretus is regarded as high compared to the outside values, albeit within the range of numbers given in the literature (Table 2.2). They indicate that the materials in the museum are effectively emitting relatively large volumes of volatile organic acids.

Table 2.2: Acetic and formic acid concentrations in Museum Plantin-Moretus (Inside Museum: Rubenszaal).[21]

	Acetic acid µg/m^3	Formic acid µg/m^3	Acetic acid ppmv	Formic acid ppmv[22]
Summer 2011 **Inside Museum**	247	60	0.100	0.031
Summer 2011 **Outside**	2	5	0.001	0.003
Winter 2012 **Inside Museum**	42	12	0.017	0.007
Winter 2012 **Outside**	7	2	0.003	0.001

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[20] (Tétreault, et al., 2003), p. 244.

[21] (Krupińska, van Grieken, & De Wael, 2013), p. 359.

[22] Conversion from µg/m^3 (a) to ppmv / 22°C (t) / =((a*22.4136*(t+273.15))/(mol*273.15+t))/1000

2.5 Historical treatments

It should be remembered that types in use were prone to many kinds of manipulation, ranging from the casting, breaking off*, dressing*, distributing, composing, printing and last but not least the cleaning of ink and re-distribution of the types. The ink and the subsequent cleaning operations in particular could have played a role in the surface reactions on the type pieces.

2.5.1 The use of inks

Two tones of ink were most frequently used: black and red. Printing inks are different in composition from writing inks. The black coloured printing inks were made on the basis of turpentine, oil and lamp black (Voet, 1969-1972) , whilst the red inks were made with vermilion or red lead. Other colours were possible: Lake and Ruffet (deeper red than vermilion), Verditur, Indico or Bice (blue colours), Orpiment, Pin, Yellow Ochre (yellows) or Verdigrease or green Verditur (greens) (Smith, 1755). Variants of black ink were in use; one was a fairly fluid kind and another much less so. In the Plantinian account-books they are found under the names '*encre faible*' and '*encre dur*'. The weaker kind would be more suitable for printing in winter temperatures (Voet, 1969-1972). In fact, the bases for making printing ink are oil varnishes. Moxon makes a distinction between the qualities of inks between England and the Netherlands ('*our Neighbours the Hollanders*'), claiming that the latter used only linseed oil with perhaps some resin ('*Rosin'*) added.

Inks in England were mixed with '*trane-oyl*' and a lot of '*rosin'* to save money. However, because of this, the ink became too thick and barely dried, resulting in pasty letters that are considered unpleasant to the eye. But also the boiling, the clearing (removing particles), the blackening (adding the black pigments) and the consistent quality of the production of ink was considered superior by the Dutch. Moxon continues to give a detailed account of the best process for making high-quality ink (Moxon, 1683).

It is unclear whether the ink or its components play a role in the corrosion development of the lead-based types. Special attention can be given to vermilion as this is a chemical composition of mercury sulphide. Hypothetically, prolonged and close contact with the lead in a humid environment could lead to the reduction of this compound, whereby the mercury could dissociate from the ink and dissolve in the lead printing letter.

2.5.2 Cleaning of types

Moxon describes how the press-man washes the type after printing to remove all the ink that is left on the surface, and the compositor rinses the letter as well as possible '*for else the Inck that is desolved among the Ly would, with long standing by, harden between the Letter, and make the Letter stick so fast together that when it comes afterwards to be Destributed, the Compositer shall not without great difficulty and trouble get them asunder. This sticking together of the Letter is call'd Baking of the Letter*' (Moxon, 1683). William Savage, a 19th-century commentator on Moxon adds, '*This [baking] is the case particularly with new letter, if it be not distributed as soon as worked off; for if it be afterwards allowed to remain some time locked up in the chase, it is very difficult to separate and distribute, and causes great loss of time, and injury to the letter*'.

Historical sources indicate that lye* was used to clean the ink from the letters and that they had to be rinsed really thoroughly or they would remain slippery for handling. He also draws attention to the fact that ‘their wetness’ affects the fingers, making them supple and therefore unfit for the nimble deposition of the letters. A piece of alum was kept in a box to be pinched now and then between the fingers, contracting the grain of the skin and the dilated pores of the fingers. Another possibility was to wet the slippery letter with water containing dissolved alum (Smith, 1755).

When letters became sticky because they were kept too long in their cases or were put up without rinsing, it was common to pour boiling hot water over them. If that had no effect after half an hour’s soaking, the ‘experiment’ was repeated. In some cases, letters are cleaned of small artefacts in their cavities with a needle of some sort (Smith, 1755). This could have led to damage on the printing face, although the workmen would certainly have tried to avoid this.

Newly cast letters that are not well dressed may have burs or other irregularities that make them stick with handling. To prevent this, they are soaked in soapy water to make them slide easily between the fingers while composing text (Smith, 1755).

The above sources form a point of discussion, since it may well be that some sticking of the letters when composed is preferred (Mosley, 1995). It prevents them from falling apart too easily or from being drawn from the lines while rolling the ink balls over the surface. These facts would explain the holes that are found in the very early type pieces, such as those from Lyon (Audin, 1954). It is supposed that a thread was fed through the holes to secure the type pieces in place after composing the lines and throughout the printing process.

In any case, whether sticking was preferred or avoided, the abundant use of lye, hot water, alum and possibly other products may all have had an effect on the printing type and the way it has been ageing, together with the storage conditions over the centuries. Since the variety and type of products and procedures are unknown, these are not studied in the current research.

2.5.3 Lining of cases

In the distribution trays at the Plantin office, paper lining is often present. Preliminary observations have shown that this proved to be beneficial for the conservation of the lead types (Storme, Jacobs, & Lieten, 2013). The motivation for the typesetters to do this is not very clear. In some cases, it was used to divide large compartments into smaller ones. For this purpose ‘blue paper’ was glued (‘pasted’) to the bottom plate before the casing arrangement was placed upon it. This paper was nevertheless not recommended because it would spread the moisture from poorly-rinsed and dried types leading to decay and sometimes warping of the boxes, resulting in separation between the bottom and the compartments. Therefore, plain unprinted writing paper was recommended, to be folded in the compartments. For small compartments, smooth wrapping paper could serve too (Smith, 1755). Lining of the cases is expected to prevent to some extent organic acids from the wooden tray coming into direct contact with the types.

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3 Methods and techniques

Content

3.1 Introduction

This chapter describes the techniques and their specifications used in this study. The main topics are metallography, corrosion development and corrosion products identification.

3.2 Metallography

Metallography is a study of the microstructure of metals and alloys. Different kinds of information can be obtained by metallography: for example, the manufacturing process, the thermal history, the composition of the metal or alloy and the physical structure of the alloy and the corrosion products. It is possible to study, for example, grain size, grain shape, grain errors, porosity and inclusions. Sampling, embedding, grinding, polishing and etching are important processes within the metallographic examination.

3.2.1 Embedding

The samples were embedded for easy handling, protection against deformation during grinding and polishing and for storage purposes. A small selection of historical lead letters were embedded with Technovit 2000 LC, a methacrylate that polymerises in blue light. The samples were placed in transparent, plastic cups so that the light could penetrate, and the acrylate hardened under a Technotray CU polymerisation machine from Heraeus Kulzer. The letters were fixed with clips and clamps, to keep them in place when pouring the acrylate in the cups, resulting in full transparent embedded samples. For the items with porous and loose corrosion products, the disintegrating letters were fixated and hardened first with Technovit 2000 LC fixing paste, before embedding. After casting the resin in the cups, each sample was coated with a 2 mm layer of varnish, in order to prevent sticking.

The samples of the newly made lead-antimony-tin alloys were embedded in room-temperature hardening methyl methacrylate resin Technovit 4004. Standard cups of 25 mm diameter were used for all items.

3.2.2 Grinding, polishing and etching

Grinding smoothens an irregular surface, so that all surface deformations are removed in this first stage of polishing. The size of abrasive grain is gradually reduced to minimise irregular damage on the surface. Grinding the samples under running water helps flush away metal particles and abrasive grains. In addition, water has a cooling effect on the sample, thus maintaining the microstructure.

Polishing is a finer form of grinding, to remove scratches from the surface. This enables an accurate metallographic interpretation. Optimal observation is ensured by removing pits, inclusions, comet tails*, stains and scratches. Before, during and after each grinding or polishing step, the samples were rinsed and dried. Contamination by grains or metal parts must be avoided, because deep scratches impede the examination. It is recommended to rinse the samples with deionised water and dry them with alcohol and hot air, so all the fluids can evaporate from the cracks and pores. If this is not done, drying spots can impede the observation.

The procedure, based on Buehler's manual (Buehler 2007), was initially used to grind and polish the samples. However, the workflow had to be slightly adapted because of the apparent embedding of particles, originating from the alumina suspension. The last steps in Buehler's standard procedure for lead (Microcloth with respectively MicroPolish II deagglomerated alumina oxide particle suspension and Masterprep 0.05 μm sol-gel alumina suspension) were omitted for this reason. Corroded lead alloy samples with (hard) antimony particles were polished to P2500.

The antimony-rich solid solution and SbSn-rich phase can often be distinguished by etching with a mixture of 0.5 M ammonium persulphate [$(NH_4)2S_2O_8$] solution (10 g in 100 mL H_2O) and 2 M tartaric acid [$C_4H_6O_6$] solution (30 g in 100 mL H_2O). The antimony-rich phase is white and remains so during etching; the SbSn-rich phase is light grey, but becomes yellowish during etching and may develop etch pits. In a fine eutectic structure, the lamellae of the antimony-rich phase are unchanged by etching, but the lamellae of the SbSn-rich phase develop dark edges. Primary crystals of the antimony-rich phase are angular, but are usually somewhat elongated; primary crystals of the SbSn-rich phase are cuboidal (ASM 1990).

Non-corroded lead and lead alloys were polished to paper P1500 and finished with a Chemomet cloth, used together with an etching solution to avoid any introduction of particles or the occurrence of smearing. The chemical etch/polishing was performed with a solution of 84 ml glycerol, 8 ml acetic acid and 8 ml concentrated nitric acid on a Chemomet I cloth (Scott 1996). This reveals the main grain structure of the metal. The samples were examined directly after etching, since the lead rapidly tarnishes again when exposed to air (Vander Voort 1999). In some cases, additional etching before microscopic examination was performed with a solution of 5% nitric acid in 95% ethanol (Mahmudi and Rezaee-Bazzaz 2005).

3.3 Optical microscopy (OM)

For the evaluation of historic type samples and their corrosion, an Olympus BX 41 optical microscope in the Heritage Department of the University of Antwerp was used. It is equipped with episcopic lenses up to 500x magnification in Brightfield and Darkfield (DF) modi.

To evaluate the experimental casts with respect to grain size and distribution, a Leica Model MEF4M with an AxioCam MR5 at the University of Genova, Department of Chemistry, Metallurgical L*a*b* was used. Images at magnifications of 25x, 100x, 200x, 500x and for some selected alloys to 1000x were recorded. A Scanning Electron Microscope (SEM, below) was also used for imaging the microstructures.

3.4 Scanning Electron Microscopy and Energy Dispersive X-Ray Spectrometry (SEM-EDX)

A scanning electron microscope (SEM) offers images of a sample by scanning it with a beam of electrons in a raster scan pattern. The electrons interact with the atoms of the sample, producing signals that are perceived by different detectors linked to a digital monitor.

The type of signals produced by SEM, quoted below, can give information about the sample's surface topography, composition, and other properties:

- Secondary electrons (SE): provide information on the surface topography of the sample.
- Back-scattered electrons (BSE): electron beam reflected by the sample, where its intensity is related to the atomic number of the specimen. This is displayed as variations in brightness on a monitor. Consequently, it gives information about the composition and distribution of the elements in the sample.
- Characteristic X-rays: identify the elements in the sample.

The latter can be done in three ways: the measurement of one point or multiple points to give a spectrum per point; line measurements that show different spectra between zones; and the measurement of every point of a surface (mapping), resulting in a diffusion image for each element.

With SEM the alloy phases can be visualised and identified. For the measurements in this study, a Quanta 350 SEM with Oxford EDXS instrument at the University of Genova was used for most of the measurements on the experimental prepared lead alloys. Internal and external calibration with cobalt, lead, antimony and tin was carried out prior to the measurements, at 20 keV. The spectra were calculated for quantitative results using the INCA software.

Additional measurements were performed with a Quanta 250 SEM with Oxford EDXS at the University of Bologna and at the University of Antwerp, Department of Physics. Specific settings are mentioned in the chapters where SEM-EDX results are shown.

3.5 Hardness measurements

For handpress-printers, the hardness of their type was of prime importance. The harder the alloy, the longer it would withstand manipulation and printing actions. For the evaluation of the hardness of the respective alloys, macro- and micro hardness tests were performed. For obtaining hardness values in the 20th century, Brinell* was often used and this data is found in older papers. For the measurements in this research, the more precise Vickers and Micro-Vickers technique was applied.

A series of Macro-Vickers hardness tests were performed on the lead alloys (see Chapter 4) at the University of Antwerp, Department of Engineering. The instrument used was a Zwick, type 3212 with a pyramidal indent and a load of 1 Kg for 20 s of impression time. Three measurements were executed for each alloy to obtain an average value.

Micro-Vickers hardness tests on a similar series of experimental produced lead alloys were performed at the University of Genova, Department of Chemistry, Metallurgical lab, using a Leica VMHT 30A, equipped with a 500x magnification for the indent location. For the macro-hardness 50 g was applied for 15 seconds, at 5 points per sample starting from the centre of the cast to the side of the cast in steps of 1 mm. The micro-hardness test was performed with 5 g for 15 seconds in the eutectic or eutectic-like areas and if applicable, separately in distinguishable phases or metallic inclusions. In some cases, these inclusions were too small to be measured separately, as for example in the alloy Pb 80, Sb 10, Sn 10 wt%. Measurements are indicated as (µ-) Hardness Vickers, HV.

3.6 Gravimetric measurements

The weight gain of corroded samples was measured with an analytical balance Ohaus, max. 300 g, 0.001 g reading (possible error max. 0.003 g). Lightweight inert plastic scoops were used to hold each of the samples, preventing the loss of non-adhering corrosion products. Each sample (about 10 g) together with its scoop (about 0.3 g) was weighed before, during and after the corrosion procedure.

3.7 Colorimetric measurements

3.7.1 UV-Vis spectrometry - CIE-L*a*b* colour measurements

UV-Vis spectrophotometry was used for the measurement of colour changes (Lafuente, et al. 2013) and the results are expressed in ΔE before and after the ageing procedures. Measurements were performed with an Avantes spectrophotometer consisting of an AvaLight-DH-S-Balanced deuterium/halogen light source and an Avaspec-2048 spectrometer. Optical fibres connect to an integrating sphere with an active diameter of 50 mm. The fibre of the light source is coupled to the illumination port at an angle of 8° to the perpendicular line, while the fibre from the sphere to the spectrometer is coupled to the measurement port at an angle of 90°. In this way, the light source directly illuminates the sample surface, while the diffuse and specular reflection is measured indirectly. UV-vis spectra between 175 nm and 1100 nm were collected with a resolution of 0.54 nm. The instrument was calibrated by collecting a dark spectrum and an emission spectrum on a reference white tile, allowing the conversion of the diffusely reflected spectrum into an absorbance or reflectance spectrum. The Avasoft software allows for the selection of a D65 illuminant and a CIE standard observer of 2° in order to calculate the L*a*b* values from the collected UV-vis spectrum. L* represents the difference in lightness and darkness (100 = white, 0 = black), a* represents the difference in red and green (+ = red, - = green) and b* represents the difference in yellow and blue (+ = yellow, - = blue). The higher the value for a* or b* is, in negative or positive sense, the stronger this colour is. Colour variations were evaluated by calculating $\Delta E = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$. Results are the average of at least three measurements.

3.7.2 Reflectance UV-spectrophotometry

With preliminary tests it was observed that pure corrosion products generate a different absorbance spectrum in the UV region between 220 and 360 nm, besides the visible colour-related spectrum curve between 360 and 800 nm. A possible relationship between the obtained spectrum and a corrosion product identification was investigated. The results generated are the average of at least three measurements. UV spectra were collected identical to the CIE-L*a*b* measurements (see 3.7.1). However not included in this thesis, UV spectra were also collected with a probe, emitting the lightbeam and receiving the reflected light at a distance of 10-30 mm, shielded from the environment with a black cover. Very similar spectra as with the diffusing integrated sphere were recorded, albeit with slightly more noise. This method was tried for possible future distant measurements on objects or environmental metal sensors.

3.8 Inductive Coupled Plasma – Optical Emission Spectroscopy (ICP-OES)

Experimental casted pieces were composed of a selection of binary and ternary lead alloys, which needed to act as references. Chemical analysis (ICP-OES) was performed to ensure their correct elemental concentrations. This was performed in the Laboratory Centro Tecnologico Sperimentale S.R.L.(CTS), Ceparana, Italy, by Dr. Lorenzo Rolla (2016).

The ICP-OES analyses were performed with the following set-up and conditions: Analytical balance: Adventurer Pro OHAUS AV2101 S/N 8728141626; Vessels for sample solution - digestion apparatus: hot plates and usual laboratory glassware - Class A; reagents (water, acids): Water ASTM D 1193 Gr. IV; all the acids are ACS Reagent Grade; acid solution of nitric, fluoroboric and tartaric acid. Standards: standard of pure Pb BCS 210; standard of Pb (BASE Sb and Sn; alloy BCS 177/2; stock solutions; for all element Ultra scientific ICP Calibration standard Cod. ICM – 103.

Emission Spectrometer: ICP-OES Optima 2000 DV Perkin Elmer equipped with autosampler AS93 PLUS and injection system nebuliser ESI Apex E. With the conditions for all elements: Apex: gas Argon T flow 0.45 l/min , sample flow 0.45 ml/min; ICP: plasma gas flow 20l/min, auxiliary gas flow 0.2 l/min, RF power 1400 W. Stabilisation time between samples: delay between samples. Reading time: time of replicates 3; selected wavelengths: Sb 206.836; Sn 189.927; Pb 220.353; Y 371.029 (Internal standard used for control and correction).

3.9 X-Ray Fluorescence (XRF)

3.9.1 Lead reference materials and historical types

Until 2016 the instrument initially used at the UA, FOW, Heritage Department was an Innov-X Systems α–4000 Portable XRF. The measuring spot has a surface dimension of about 1 cm^2 and reaches in solid metals a maximum depth until about 100 µm, depending on the metal or alloy. Analytical Mode 0-40 keV, measurement time 100 s. Built-in Innov-X software was used to gain wt% results from the obtained spectra. At the end of 2016 this instrument was replaced by a newer model, an InnovX-Olympus Delta with a highly sensitive CCD, enabling shorter measurement times compared to the Innov-X Systems α–4000.

The quantification precision was checked using a set of lead-antimony (-tin) alloys. These were in turn controlled for their correct composition at the CTS labs (see 3.8); for the comparison with the ICP-OES measurements a Niton XL3t 980 Goldd+ Matr. 83128 and Software program ‘all metal’ were used.

3.9.2 Copper matrices measurements

The analytical measurements on later lead samples, but primarily on the copper matrices, were executed in situ with an X-Ray Fluorescence instrument, Olympus-InnovX Delta Professional (40 keV, 20 sec. live Time for each measurement). The software used for calculating the quantitative data from the spectrum was Innov-X Delta Advanced PC Software. Measurements were taken on the cleanest side of each piece; for the strikes this was the upper face, for the matrices this was mostly a side or the backside, free of inks or other remnants from printing. The quantification of the elements was verified with measurements on IMMACO standard copper alloys.

3.10 Raman spectroscopy

Micro-Raman analyses for the identification of lead corrosion products were performed with a Renishaw Invia coupled with a Leica DMLM microscope (Objective Leica N Plan L 50x/0.50 l.f.) at the University of Antwerp. The excitation source was a near IR diode laser (λ = 785.0 nm, full power 500 mW, reduced to 10% resulting in an effective 6.2 mW on the sample). Spectra were recorded from 4000 to 100 cm^{-1} spectral resolution. Integration time was 10 seconds and three accumulations were used on each sample.

3.11 X-Ray Diffraction (XRD)

X-ray diffraction (XRD) is a versatile, rapid analytical and non-destructive technique that reveals detailed information about crystallographic structure, chemical composition and physical properties of natural and manufactured materials.

For the current study, the μ-XRD reflection measurements were performed at the University of Antwerp, Chemistry Department. The instrument is used in scanning mode, implying an IμS-Ag^{HB} X-ray source and a Pilatus 200K area detector with 2° incident angle between sample and beam. Beam size was ~ 3 x 0.1 mm^2 (h x v) (estimate) at an energy of 22.162 keV (Ag-K_α). All results were matched with the ICDD (International Crystallography Diffraction Database).

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4 Lead type: production, microstructure and chemical composition

Publications related to this chapter:

Storme P. '*Historical Type in the Collection of the Museum Plantin-Moretus*', in: Tijdschrift voor Mediageschiedenis Vol. 19, No 2 (2016) in the theme issue: Typografie in mediahistorisch perspectief, p.1-15.

Storme P., Selucká A., Rapouch K., Mazík M., Vanmeert F., Janssens K., Van de Voorde L., Vekemans B., Vincze L., Caen J., De Wael K. '*Composition and corrosion forms on archaeological and non-archaeological historic printing letters from the Moravian Museum, Memorial of Kralice Bible, the Czech Republic and the Museum Plantin-Moretus Antwerp, Belgium'* in: La conservation-restauration des métaux archéologiques : des premiers soins à la conservation durable, Namur, Institut du Patrimoine wallon (2015) p. 59-65.

Content

4.1 Introduction

From the 15th to the 18th centuries, handpresses and movable type were used for book-printing. There is relatively little known about historical lead-based types, from a material point of view. Lead-based alloys are generally known to be used for casting type, at least since the 16th century. In the earliest times of handpress printing, alloys would have been more tin-based as some archaeological evidence and historical sources suggest (see Chapter 2). Although there are some fair descriptions about the composition of lead type (Carter, 1960), there is little systematic research available to clearly describe the lead alloy compositions used in the earlier days of printing. From the 19th century on, there are a large number of specified alloy compositions because they were developed for semi-automated casting machines such as Monotype, Linotype, etc. The use of lead-based alloys to produce type continued until offset, photographic and digital methods replaced them around the 1960s.

Cast lead type is often regarded as of secondary interest to historic researchers since it can only be produced by means of matrices, which are in turn produced by using steel punches. The question of lead type authenticity is posed along with it, since lead type could have been recast at any time in history. While it is necessary to consider these very important facts, an in-depth study on a materials base might provide new evidence. Generally speaking, handbooks mention lead, tin and antimony as the composite elements for historical type, but in fact little is known for certain about the different metal components used in the 15th and 16th centuries. This chapter focuses on the alloys of historical type preserved in the MPM. A methodology and a measuring technique to apply to the alloys are proposed in order to survey surviving pieces of type. Up until now, material-based research has never been performed on a wide scale. There are reasons for the scant interest in the material, not least the fact that chemical analysis could only be performed by destructive, slow and costly methods of analysis in past decades. Today, analytical instruments such as XRF provide the opportunity to measure large numbers of metal objects in a relatively short period of time and in a totally non-destructive way.

Communicating with a number of historians, it appears that there are many things about lead type that are unknown or at least unclear. To offer more specific information about lead type alloys and their specifications, it seemed useful to study them from a metallurgic point of view.

Production techniques, theoretical compositions and some existing compositions of historical type are presented in Chapter 2. In this chapter, analytical measurements on types from the MPM collection were performed to obtain a broader understanding of the variation in compositions and possible tendencies over time. Additionally, accurate measurements that can be performed in situ are also beneficial to distinguish the lead-antimony alloys, which are more prone to corrosion, in contrast to the lead-antimony-tin alloys that are more stable in the historical museum environment (Storme, Jacobs, Lieten, & ., 2013).

4.2 Experimental: alloys, analytical techniques and selection of type pieces

Lead-based alloys are rarely used today because of their toxicity. Consequently, there are less standardised alloys available as reference materials for the study of historic type metals (alloys especially designed for producing printing letters, i.e. 'type'). A few exceptions can be found in ammunition (lead-antimony alloys for bullets) and lead-based bearing* alloys. The National Institute of Standards and Technology (NIST) lists one alloy (SRM 1132) that is a lead-based bearing metal with a composition of Pb 84%, Sb 10% and Sn 6% (mass fraction %).[1]

In order to perform tests on element determination and distribution, phase recognition, hardness values and corrosion development under different circumstances, a selection of alloys was cast.

4.2.1 Experimental alloy casts

4.2.1.1 Alloy selection

A selection of Pb, Sb and Sn alloys was made, based on three major observations. The prime selection criteria were, firstly, the alloy element ratios as found in the historic literature on the subject and as stated in contemporary literature sources (Osamura, 1985). Secondly, data was derived from the analytical measurements performed by various researchers, including own measurements. Thirdly, the ternary phase diagram of Pb-Sb-Sn, within the range of a maximum of respectively Sb 20 and Sn 12 weight percent (wt%), shows three major areas (Fig. 4.1). A ternary eutectic point is located at Pb 84, Sb 12, Sn 4wt% (Fig. 4.1; E in Fig. 4.2) whilst a pseudo-binary eutectic point is situated at Pb 80, Sb 10, Sn 10wt% (245°C in Fig. 4.2). The eutectic point of the binary alloy Pb/Sb is situated at 11.2wt% Sb (251°C at point $e_{Pb\text{-}Sb}$, in Fig. 4.2).

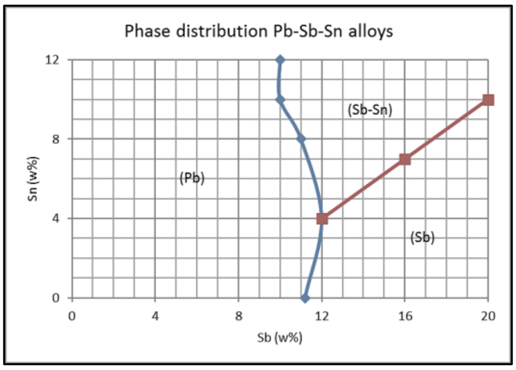

Fig. 4.1: Main phases present in the lead-based alloys with Sn and/or Sb additions.

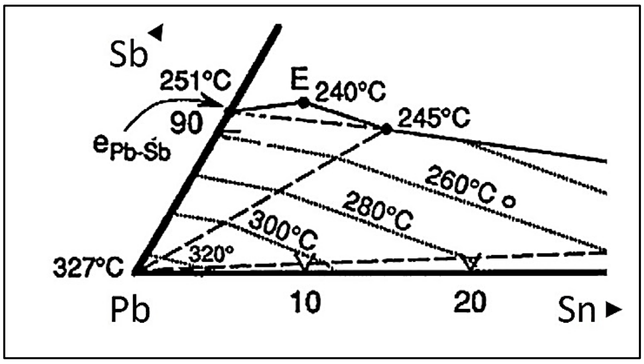

Fig. 4.2: Detail of the lead-rich corner of the Pb-Sb-Sn ternary phase diagram.[2]

Based on these observations, a selection of alloy compositions was made, covering the ternary lead alloys compositional grid ranging from 0 to 20wt% Sb and from 0 to 12wt% Sn, in steps of 4wt%, including an additional pseudo-binary eutectic alloy of Pb 80, Sb 10 and Sn 10 wt%, resulting in a total of 16 alloys, Pb included (Table 4.1).

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[1] NIST website: https://www-s.nist.gov/srmors/view_detail.cfm?srm=1132; consulted 16.1.2017

[2] (Krane, 2004), p.99

Table 4.1: Selected alloy compositions for Pb, Pb-Sb and Pb-Sb-Sn ratios.

wt%	**Sb 0**	**Sb 4**	**Sb 8**	**Sb 12**	**Sb 16**	**Sb 20**
Sn 0	Pb 100	Pb 96	Pb 92	Pb 88	Pb 84	Pb 80
Sn 4			Pb 88	Pb 84	Pb 80	
Sn 8			Pb 84	Pb 80	Pb 76	
Sn 12			Pb 80	Pb 76	Pb 72	

4.2.1.2 Experimental casting properties

The casting of these newly made alloys was performed under controlled specifications of melting temperature, low-oxidising atmosphere, a standardised way of casting, the choice of mould material and the cooling rate (Garmong, 1972) (Krane & Incropera, 1997). This was important for homogenising the alloys, standardising the casting results and reproducing historic handcasting properties as closely as possible.

First, a master alloy of Pb 80 and Sb 20wt% (Roumina, Raeisinia, & Mahmudi, 2004) (Mahmudi & Rezaee-Bazzaz, 2005) was produced to optimise the Sb distribution in the lead matrix. Sb has a high melting point (817°C) compared to Pb (327°C). Consequently, Sb had to be melted first and Pb was added while the overall temperature was lowered. The theoretical melting temperature for the master alloy is approx. 330°C. For this purpose an electric furnace with a graphite crucible was used (Fig. 4.3) at an initial temperature of 900°C to melt the antimony, and reduced to 750°C for the master alloy to be cast into bars. After cooling, this alloy was molten and cast again for homogenisation purposes.

The alloys were cast in variations of 4 wt% steps for the Sb and Sn content, as listed in Table 4.1. The alloys were composed by weighing the alloying elements as the weight percentage (wt%) of each alloy indicates. These alloys were composed from the master alloy Pb 80 Sb 20wt% and calculated for the respective addition of Pb and/or Sn to the required composition. The metals were put together and molten in an electric furnace inserted with a graphite crucible, set at a constant temperature of 375°C. For each of the alloy groups (i.e. pure Pb, Pb-Sb and Pb-Sb-Sn) another crucible was used to avoid contamination and minimise alloy composition deflections.

The ingot (mould) consisted of a two-part dense graphite bloc with an ingot capacity of 10 mm dia. and 30 mm depth (lower two-part mould in Fig. 4.4). Prior to the casting the ingot was kept in a furnace at 40°C to ensure identical cooling rates for all casts. This temperature avoids humidity on the ingot, but may also resemble the working conditions of the ingots used by the letter casters. Since it is stated that these casters deployed a constant rhythm of casting letters, up to 3000 per day, it can be assumed that after a start-up time, the mould ingot material levelled to a certain temperature. This temperature is the result of an equilibrium between the cast metal temperature, the cooling time upon opening the ingot for releasing the cast letter and reclosing the ingot to prepare for the next cast. The ingots at the time were manipulated by hand, so a rather low temperature can be assumed. This temperature also reduces the chance of Sb segregating from the Pb on cooling. It is known that measured deviations in Pb-Sb alloys up to 15% Sb might be caused by a lack of equilibrium in the samples on account of the effect of the casting conditions or the chemical composition (Hidnert, 1936).

Fig. 4.3: Left: electric furnace with closed lid to minimise oxidation and on the right hand side the graphite ingot moulds.

Fig. 4.4: Detail of the graphite mould for the cylindrical 30 g castings.

Each of the experimental casts weighted between 25 and 30 g, which also resembles the weight of medium heavy letters. The castings resulted in small cylinders of 10 mm diameter and around 25 mm in length. Slices of approx. 3 mm thickness were cut from the cylinders using a water- cooled low speed diamond-cutting wheel. These disks were required for the next experimental phases.

For atmospheric tests another series of the same alloys was cast under the same conditions but in a larger graphite mould (Fig. 4.4), forming sheets of about 50 x 80 mm in size and 4 mm thickness. From these castings, squares of 15 x 15 mm at 4 mm thickness were cut using a low speed band saw.

4.2.2 Selection of historical lead type

A first selection of types from a wide timespan (i.e. 1553-1825) was made. The items are specified in Table 4.5. The primary motivation for this selection was to establish a first view on compositions and variations throughout the 16th until 19th century within the MPM collection.

A second selection of historical type from the MPM collection was made. Lead type items of Ethiopean, Hebrew, Fleuron and Music were chosen as they can represent the early days of printing at the MPM, i.e. 16th century. The selection is presented in Table 4.2. It concerns six groups of type with a total of 28 items that were measured with XRF, twice for each item. The types were selected because they were used within a limited time-frame and it is therefore believed that there is only a slight chance that they were recast in later times. The relevant data for this chapter is retrieved and presented here to complement other results.

Table 4.2: Selected type for XRF measurements on the alloy compositions.

Inventory	Cutter	Date	Name	Old corpus name	Punches N°	Matrices N°	Types
ET 1	Unknown (Hand B)	1591-1597	Ethiopean	Tekst (142 mm)	ST 59	MA 73a	1-5
H 2	Unknown	1564	Hebrew	Double Augustine (120 mm)		MA 34	1,2
FL 3	van den Keere	1574-1578	Fleuron	2 regelen Mediaan	ST 76 b	MA 188 b	1
FL 3	van den Keere	1574	Fleuron	Parangon	ST 76 c	MA 188 d, e	2
FL 3	Granjon	1567	Fleuron	Text		MA 188 f, g	3
FL 3	Granjon	16th C	Fleuron	Philosophie			4,5
MU 3	van den Keere	1573	Petites notes pour les processionales		ST 66	MA 88	1-5
MU 6	van den Keere	1571	Moyennes notes du Missel		ST 65	MA 87	1-5
MU 9	van den Keere	1577-1578	Moyenne musique		ST 70	MA 100	1-5

A third and final selection within the scope of this study was made for the following items respectively: Hebrew, Syriaque, Samaritain and Ethiopean type (16th century), Initials 'Cadeau' with grotesks (1575), wooden characters that were copied in metal, such as inventory nos. ST 1 (1575), ST 3 (1565-1571), ST 79 (1578), ST 80 (1577) and 'Initials Roman I with religious scene' (1850). These large format lead types represent particular and rare items in the MPM collection, complementary to 'plain text' types.

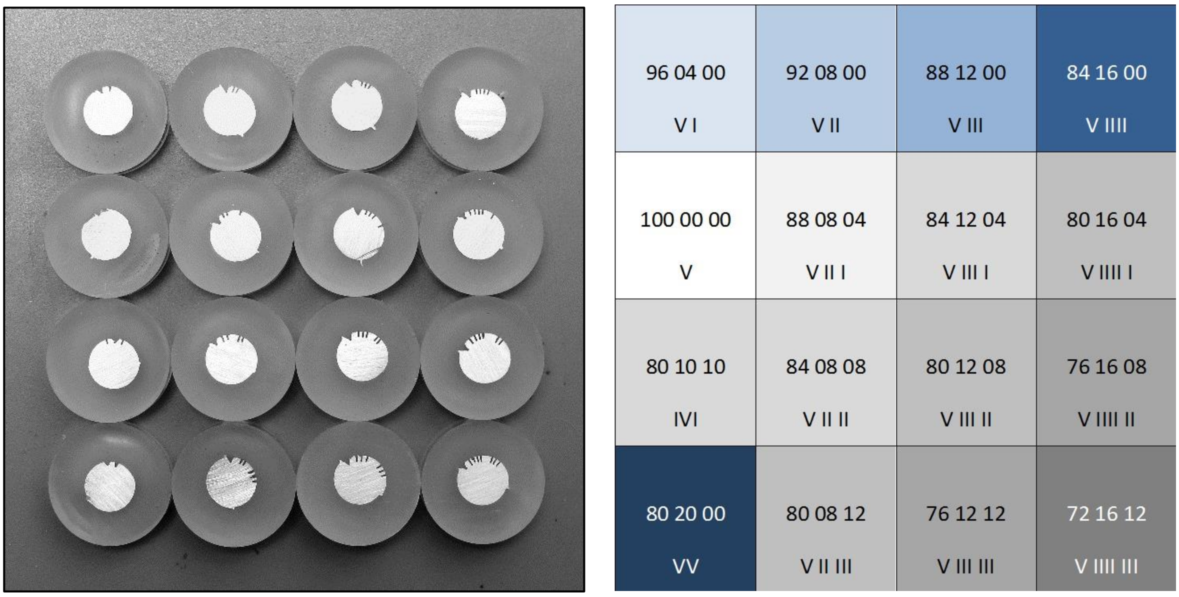
Additionally from this early period, a series of brass ornaments were also examined to complement the view on metal compositions that were used as printing matter in the 16th century, or at least are assumed to be from that period (see 4.3.2.3.9).

4.3 Results

4.3.1 Experimental alloy casts

The reference alloys produced were numbered using a numeric order of wt% Pb-Sb-Sn. As an example, an alloy indicated as ‘76 16 08’ thus corresponds to 76 wt% Pb, 16 wt% Sb and 8 wt% Sn.

Additionally, indentations were made on the rim of each disc to avoid accidental mix-ups. The marks were coded as follows: a ‘V’ for Pb, with next to it a saw line for every step of 4 wt% Sb. If Sn was also added to the alloy, next to the Sb lines a new saw line was applied for each step of 4 wt% Sn, leaving some space between the two groups of lines. The above example of coding gave as indentation marks: V IIII II. All alloys were marked in this way, except for two: Pb 80 Sb 20 wt% was indicated as ‘VV’ and Pb 80 Sb 10 Sn 10wt% was indicated as ‘I V I’.

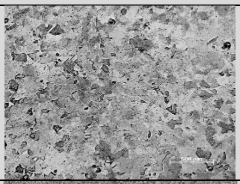
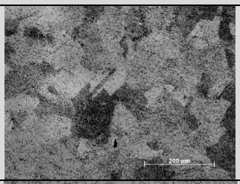
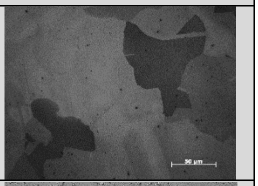
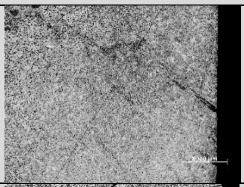
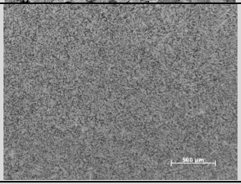
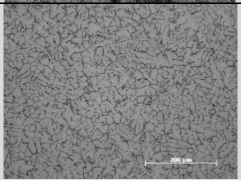
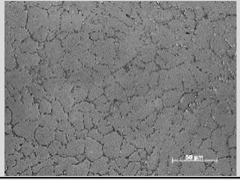
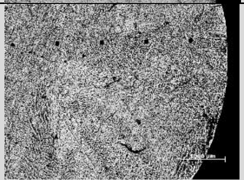
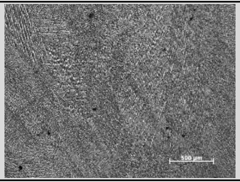
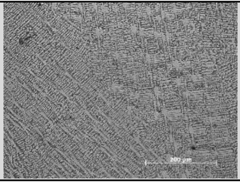
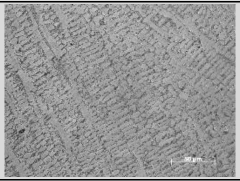
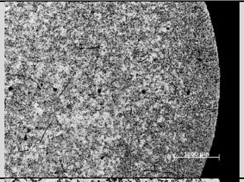
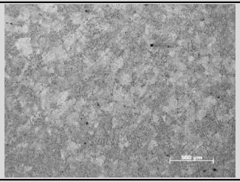
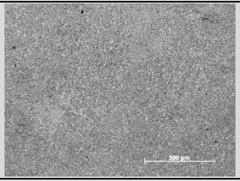
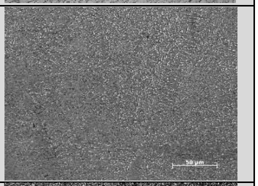
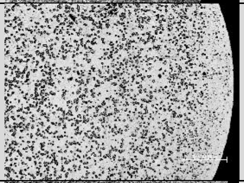
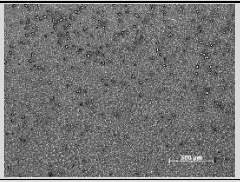
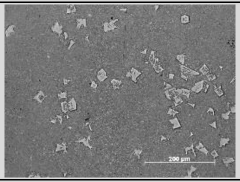
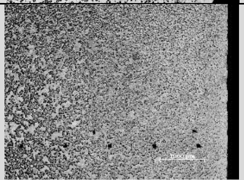
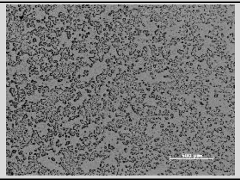
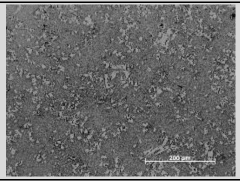
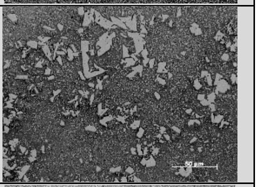
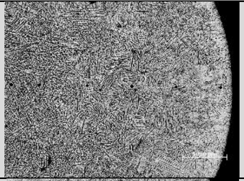
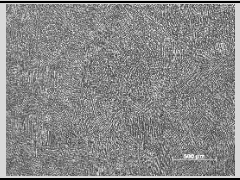
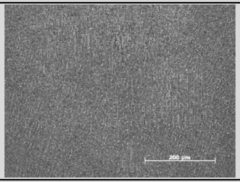
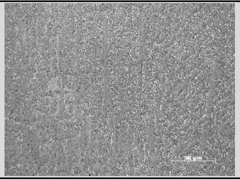
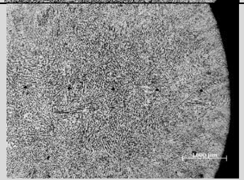
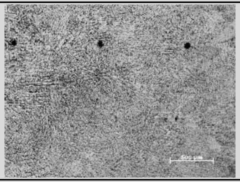
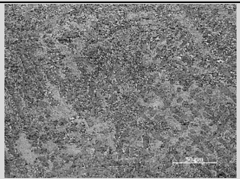
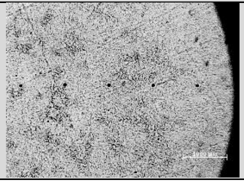
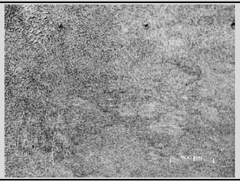
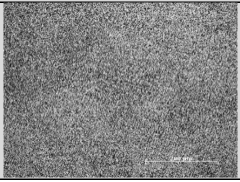
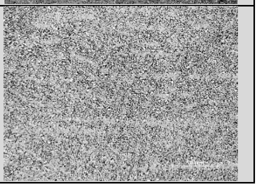


96 04 00 V I	92 08 00 V II	88 12 00 V III	84 16 00 V IIII
100 00 00 V	88 08 04 V II I	84 12 04 V III I	80 16 04 V IIII I
80 10 10 IVI	84 08 08 V II II	80 12 08 V III II	76 16 08 V IIII II
80 20 00 VV	80 08 12 V II III	76 12 12 V III III	72 16 12 V IIII III

Fig. 4.5: Left: Alloy discs with specific identification indentations, set in resin for polishing and examination purposes. Right: scheme with the corresponding numeric and indentation codes. Blue squares are binary Pb-Sb alloys; grey squares are ternary Pb-Sb-Sn alloys.

4.3.1.1 Metallography of the castings

The images of the cast structures show a regular distribution of phases in most cases. Some alloys display a somewhat smaller grain size at the edge of the cast piece in comparison to the centre part. This effect is due to the faster cooling rate at the ingot interface and in relation to the element distribution, i.e. eutectic or eutectic-like alloys show a sudden solidification, hence a more evenly distributed structure. As shown in Fig. 4.6: Microscopic images of all 16 alloys including pure Pb, at magnifications of 25x, 50x, 200x and 500x, optical microscope, bright field view. the metallographic structures vary greatly in relation to the tin and/or antimony concentrations. The distribution of antimony crystals and the formation of phases is discussed together with the results of the SEM-EDX analyses.

Alloy **Pb Sb Sn**	**25x** Scale bar 1000 µm	**50x** Scale bar 500 µm	**200x** Scale bar 200 µm	**500x** Scale bar 50 µm
100 0 0				
96 4 0				
92 8 0				
88 12 0				
84 16 0				
80 20 0				
88 8 4				
84 8 8				
80 8 12				

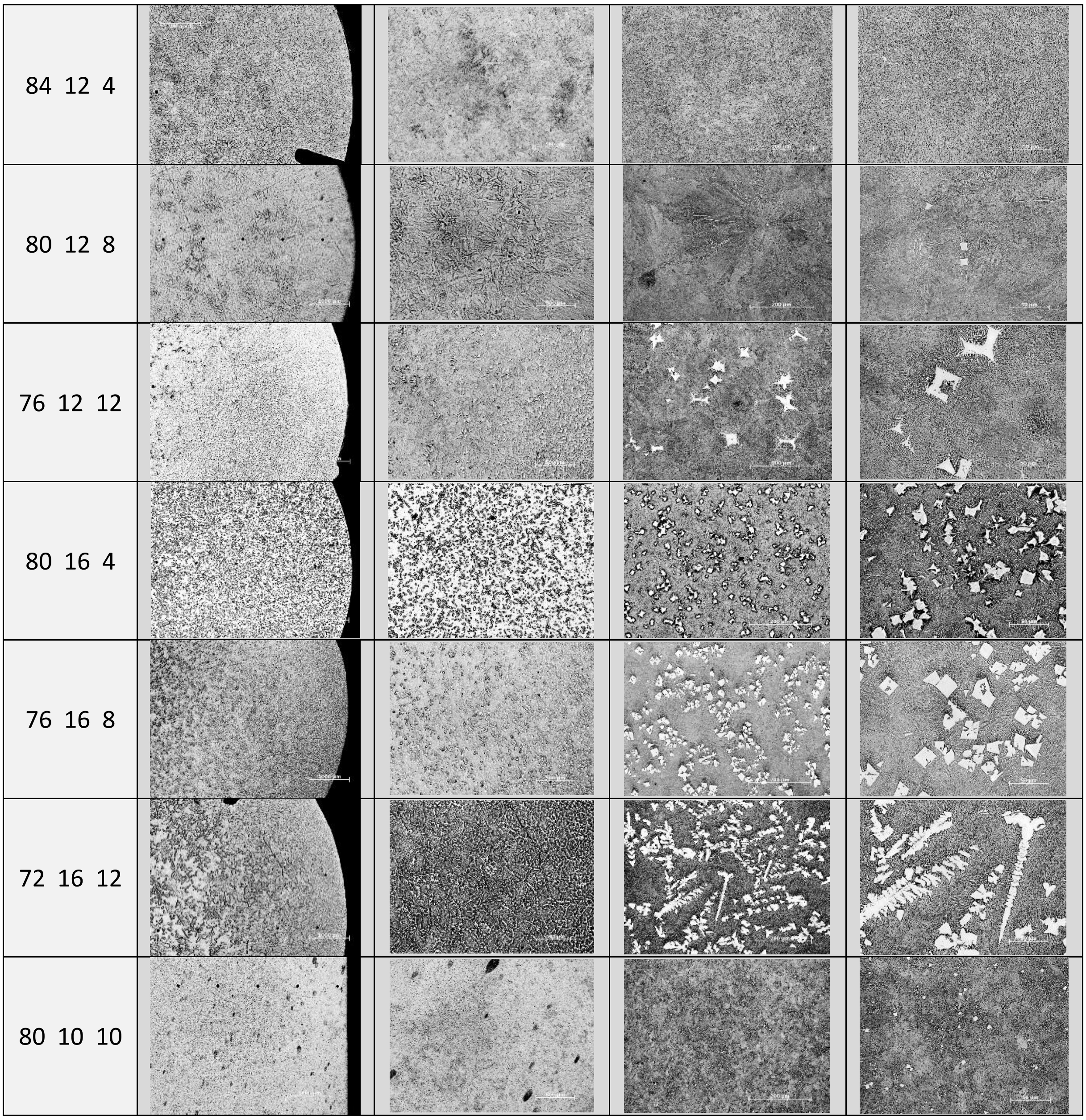


Fig. 4.6: Microscopic images of all 16 alloys including pure Pb, at magnifications of 25x, 50x, 200x and 500x, optical microscope, bright field view. Alloy element concentrations are indicated as explained in 4.3.1.

4.3.1.2 Hardness measurements

Hardness of type metal alloys is a very important factor since it defines the sustainability of the type while printing often thousands of sheets. High alloy hardness was therefore one of the primary properties the letter casters tried to achieve, besides the necessity of acquiring sharp and truthful letters. Hardness measurements of type metal alloys are available from the literature, although the data is often dispersed or merely according to the particular type alloys for Monotype, Linotype or other more recent letter casting systems. Therefore, it was deemed beneficial to perform hardness measurements on the collection of type reference alloys within this research.

Pure lead has a hardness value of about Brinell 7. Adding 16% tin to the lead increases the hardness to about Brinell 10, a gain of some 45%. The addition of 10-15% antimony to lead increases hardness values from Brinell 7 to 17, almost 250% higher than the initial lead hardness. When 8% tin is added to a 15% antimony alloy, the hardness values are further increased to Brinell 22, 315% more than pure lead. When 2% copper is also added to a lead (62%)- antimony (25%)- tin (12%) alloy, a Brinell hardness of 35 can be reached, 7 times the hardness of lead (Fig. 4.7). Some examples of type alloys are presented in Fig. 4.6, where the presence of antimony crystals is prominent in the lead matrix (i.e. all alloys with <16 wt% Sb) (Thompson, 1930).

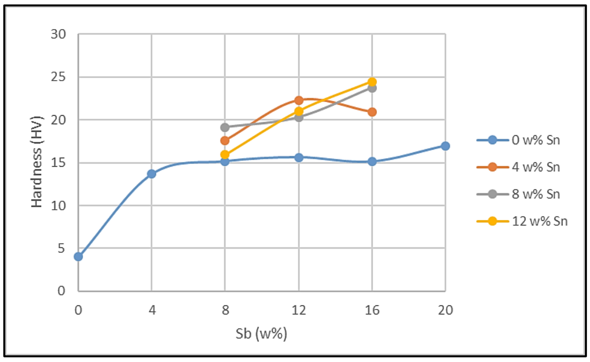


Fig. 4.7: Vickers hardness (HV) on the series of Pb-Sb-Sn alloys.

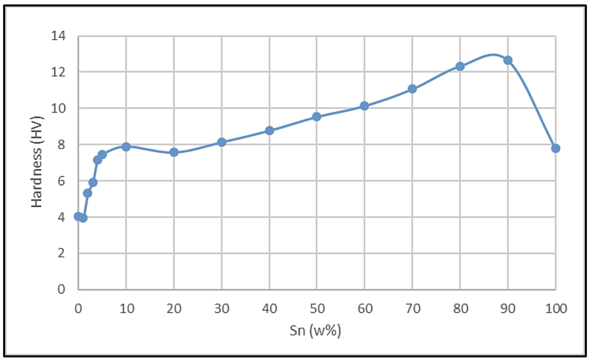


Fig. 4.8: Vickers hardness (HV) on Pb-Sn alloys.

The results of the measurements are congruent with former data on type alloys. The initial low hardness of Pb (Hardness, Vickers: HV 4) rises fast with the addition of Sb to HV 15 when 5 wt% is added. This hardness level is maintained up to a content of 16 wt% Sb and then rises slightly up to HV 17 when 20 wt% Sb is present in the alloy. For the ternary alloys where Sn is also present, a further increase in the hardness values is measured, especially when at least 8 wt% Sn is added to a lead alloy that contains at least 12 wt% Sb. The ternary alloys have values of HV 20-25 (Fig. 4.7).

Micro-Vickers hardness was also applied to the series of Pb-Sb-Sn alloys to evaluate in a more detailed way the hardness values of the different phases. The values obtained are divided into two groups, eutectic or eutectic-like alloys on the one hand and alloys with eutectic or eutectic-like matrix including distinguishable Sb or SbSn crystals on the other (Fig. 4.9). It is clear that all hyper-eutectic Pb-Sb alloys show Sb crystal segregation from the Pb-rich matrix. The difference in hardness is prominent since the crystals prove to be up to six times harder than the lead-rich matrix (e.g. alloy Pb 84, Sb 16, Sn 0wt%, shown in the graph as pairs of results in red and orange). Alloys with a high rate of Sb and Sn also show crystal segregation, as seen with the alloys Pb 80, Sb 10, Sn 10 and Pb 76, Sb 12 and Sn 12wt% (see Fig.

4.6). The crystals in the pseudo-eutectic alloy are however too small to be measured separately, hence there are no distinct values listed. No consistent tendency in increasing or decreasing hardness values can be stated in relation to the grain size or phase distribution in the centre compared to the outer sides of the cast alloys (see Table 4.3, section 'Centre to border', 5 consecutive measurements). The ternary eutectic alloy (84-12-4) shows the highest homogeneity, as expected. Alloys with the largest Sb-crystals show the highest deviations. Variations in hardness values are most probably due to indentations in the eutectic (-like) matrix or on an Sb (-Sn) crystal at or just below the surface.

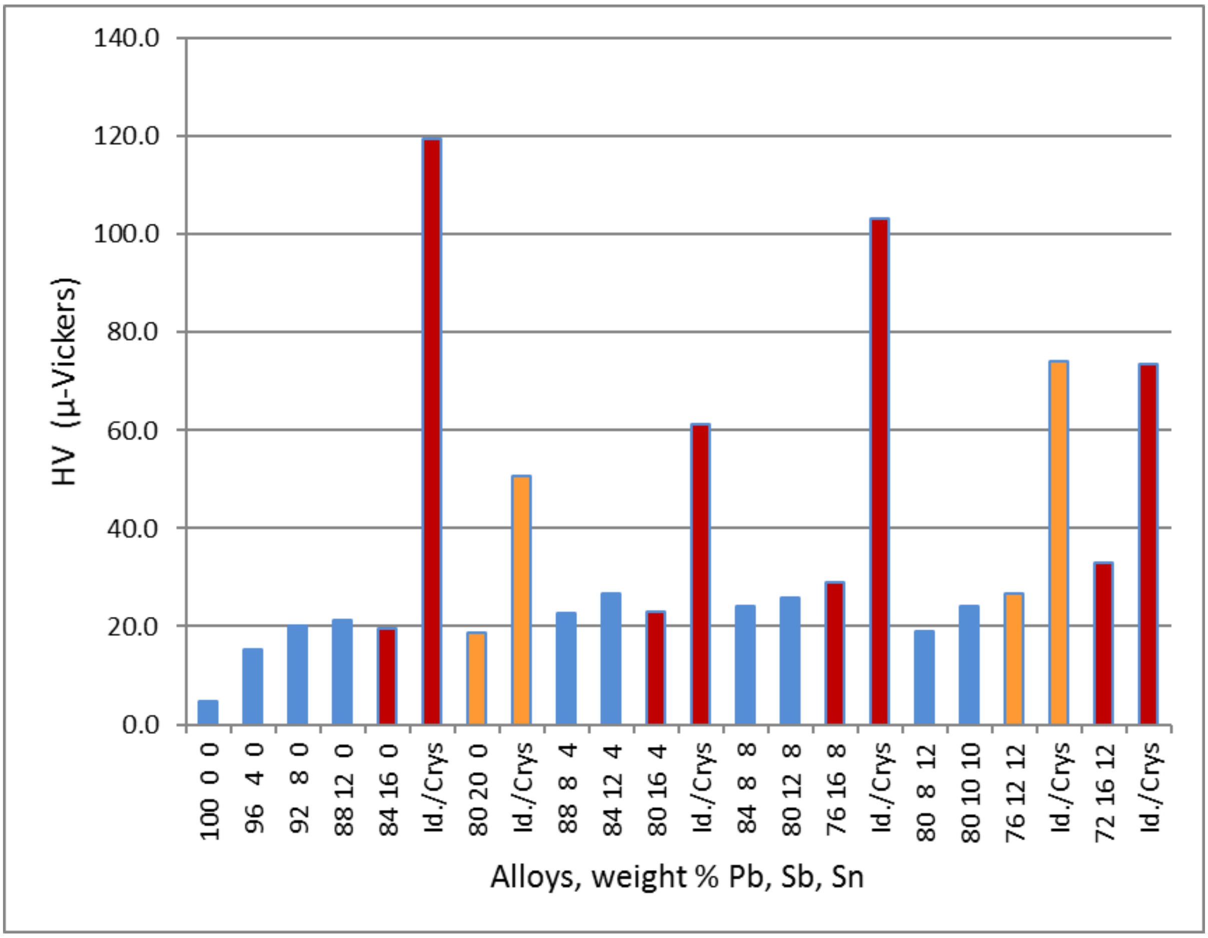


Fig. 4.9: Hardness measurements of the 16 selected alloys, in HV values. Blue is for homogeneous alloys, representing 1 hardness value; pairs of values in red and orange represent first the matrix value followed by individual measurements on the crystals, present in the matrix (denoted as 'Id./Crys').

Table 4.3: Averaged hardness values in Vickers of all alloys are given. Deviations between five consecutive measurements from the centre towards the outer edge of a cast specified (section ‘Centre to border’). Deviations are listed and the relative difference is expressed as a percentage.

Pb	Sn	Sn	HV Average	Centre to border					Dev.	Rel. %
				1	2	3	4	5		
100	0	0	4.7	4.9	4.5	5.2	4.5	4.6	0.2	5.2
96	4	0	15.3	16.1	16.9	14.9	13.5	14.9	1.0	6.5
92	8	0	20.3	20.2	19.1	20.2	21.3	20.5	0.5	2.5
88	12	0	21.4	20.9	23.8	22.3	20.0	19.9	1.3	6.2
84	16	0	19.5	23.5	19.1	18.6	18.3	18.2	1.6	8.1
80	20	0	18.7	20.9	18.5	17.2	17.8	19.1	1.0	5.6
88	8	4	22.7	21.0	23.4	25.4	20.2	23.3	1.6	7.3
84	12	4	26.6	26.5	26.8	26.9	26.5	26.4	0.2	0.7
80	16	4	23.0	22.4	21.9	23.2	24.1	23.3	0.7	2.9
84	8	8	24.1	23.4	24.7	24.6	23.2	24.7	0.7	2.7
80	12	8	25.8	31.2	23.9	24.8	23.1	26.0	2.2	8.7
76	16	8	28.9	26.6	29.9	28.1	30.8	29.0	1.2	4.2
80	8	12	18.9	19.9	17.0	20.0	17.8	19.7	1.2	6.3
80	10	10	24.0	24.2	24.8	23.1	23.2	24.9	0.7	3.0
76	12	12	26.7	25.0	25.7	24.9	33.2	24.8	2.6	9.7
72	16	12	32.9	27.4	30.1	38.8	37.2	31.2	4.0	12.3

Additionally, the hardness of Pb-Sn alloys was measured since these alloys were most probably used in the very beginning of handpress printing, by Gutenberg (°c. 1397 - †1468) and his successors. Although there is no hard evidence for this, there are many indications for this hypothesis (see Chapter 2). A set of measurements within this research frame may bring clarity to the relationship of hardness values between these group of alloys without antimony and the later alloy compositions, which all contain antimony. It is clearly shown that tin only benefits from an addition of lead between 10 and 20 wt% (see Fig. 4.8). Such alloys increase in hardness from HV 8 to HV 12-13. This is however not a significant rise compared to the explicit hardening effects of adding antimony to the alloy (giving HV values around HV 20). It is therefore very probable that a small amount of copper (Cu) was added to increase the hardness values, as the pewterers* already did in those days to enhance the durability of their tin goblets or plates. Since the printing process is very demanding for the type, this addition of copper may also not have been enough and therefore the introduction of antimony was a logical step in the evolution towards the most optimal alloy composition at the lowest possible cost.

4.3.1.3 Composition evaluations by Inductive Coupled Plasma analysis

It is known that X-ray based analytical techniques are not the primary choice for quantifying elemental concentrations of lead containing alloys. Since these techniques are semi-quantitative, they often show large deviations compared to the actual alloy compositions because of the high absorption rate of lead. Therefore, the composition of the lead-based alloys was checked with Inductive Coupled Plasma Optical Emission Spectroscopy (ICP-OES)[3].

Within the total of 16 alloys, 14 showed only a deviation between 0.0 and 0.2 wt% for the Sn and Sb concentrations respectively. The two remaining alloys, 'Pb 88 Sb 8 Sn 4' with 0.3 wt% off for each element and alloy 'Pb 80 Sb 10 Sn 10', which has an offset for Sn of 0.8 wt%, are less exact but stay below a 1 wt% deviation (Table 4.4). In conclusion, for the experiments in this research, the alloy compositions can be regarded as sufficiently accurate to be used on the one hand as representative reference materials for the calibration of XRF and SEM-EDX quantification software in this chapter, and on the other for the atmospheric experiments to follow.

Table 4.4: Concentrations of Sb and Sn in Pb alloys, by ICP-OES.

Alloy numbers	Elements wt% theoretical			Elements wt% by ICP-OES			Deviation	
	Pb	Sb	Sn	Pb	Sb	Sn	Sb	Sn
100 0 0	100	0	0	100.00	0.00	0.00	0.0	0.0
96 4 0	96	4	0	95.80	4.20	0.00	0.2	0.0
92 8 0	92	8	0	91.89	8.11	0.00	0.1	0.0
88 12 0	88	12	0	88.05	11.95	0.00	0.1	0.0
84 16 0	84	16	0	84.16	15.81	0.03	0.2	0.0
88 8 4	88	8	4	87.46	8.26	4.28	0.3	0.3
84 12 4	84	12	4	84.06	11.86	4.08	0.1	0.1
80 16 4	80	16	4	79.96	15.87	4.17	0.1	0.2
84 8 8	84	8	8	83.75	8.18	8.07	0.2	0.1
80 12 8	80	12	8	80.03	11.89	8.08	0.1	0.1
76 16 8	76	16	8	76.27	15.79	7.94	0.2	0.1
80 8 12	80	8	12	79.85	8.20	11.95	0.2	0.1
76 12 12	76	12	12	75.97	11.94	12.09	0.1	0.1
72 16 12	72	16	12	72.46	15.77	11.77	0.2	0.2
80 10 10	80	10	10	79.18	10.02	10.80	0.0	0.8
80 20 0	80	20	0	79.90	20.10	0.00	0.1	0.0

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[3] ICP-OES executed by: Centro Tecnologico Sperimentale S.R.L., Ceparana, Italy, Dr. Lorenzo Rolla (2016)

4.3.1.4 X-Ray Fluorescence analyses

X-Ray Fluorescence (XRF) is a very important tool in research on cultural heritage objects because of its ease of use in situ, speed of measurement and non-destructive character. However, since X-ray based analytical techniques are sensitive to the high absorption rate of lead, the software that is used to calculate concentrations from the spectra can be inaccurate. To evaluate the values obtained from the instrument and the software, the set of 16 alloys was measured with an InnovX α-4000, a Niton XL3 and an Olympus-InnovX Delta portable instruments. The given values are the result of a 200 s total measurement time, live time 105-110 s on an area 1 cm^2 for the InnovX α-4000. The measurements with the Niton XL3 did not come with measurement time data. The Olympus-InnovX Delta measurement was performed at 100 s live time, spot size approximately 1 cm^2.

For the purpose of conservation, it is much better if quantitative values are obtained straight from the instrument and its built-in software programme, since conservators-restorers do not always have the background knowledge to evaluate the spectral results with external software such as b-Axil. In addition, this step to acquire the quantitative data is time consuming, which would also be a drawback for its use in practice. For these reasons, an evaluation of the instruments and the built-in software is made based on the produced set of reference alloys.

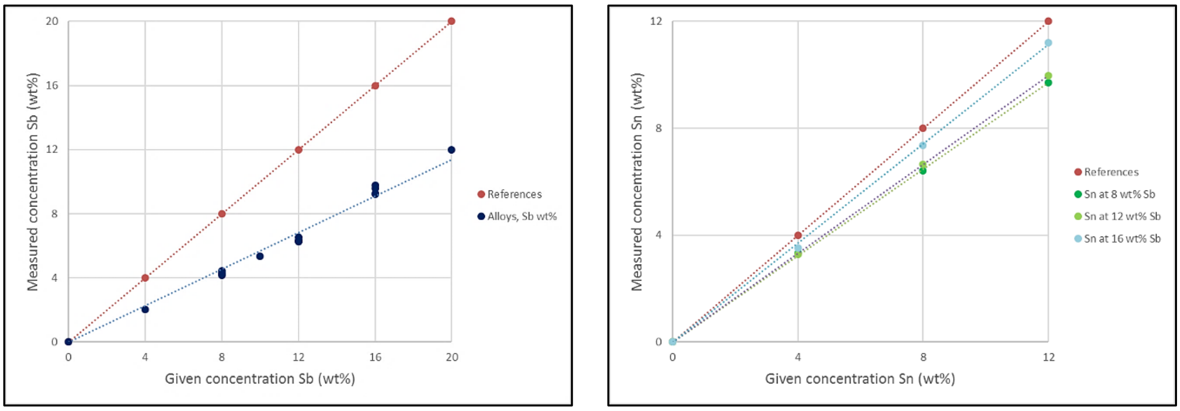


Fig. 4.10: Results of the InnovX α-4000 XRF instrument and included software programme: left image Sb concentrations in Pb-Sb alloys; right image Sn concentrations in Pb-Sb-Sn alloys. Red dots indicate the given concentrations; others are the generated concentrations by the instrument and software.

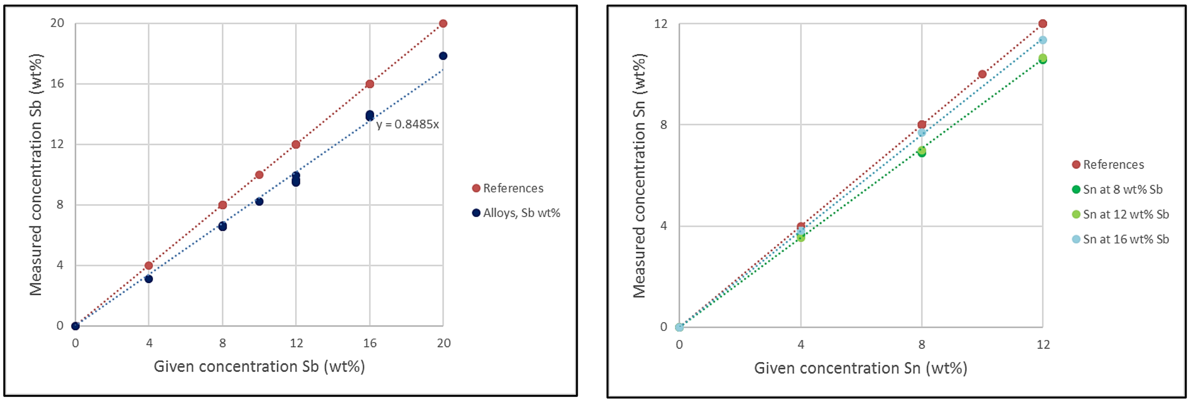


Fig. 4.11: Results of the Niton XL3 XRF instrument and built-in software, used by the CTS lab (Italy). Left image Sb concentrations in Pb-Sb alloys; right image Sn concentrations in Pb-Sb-Sn alloys.

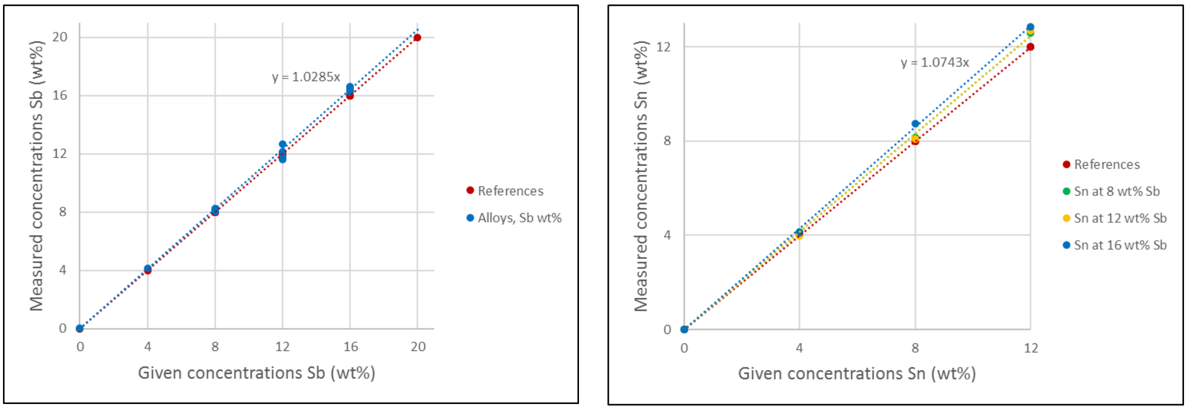


Fig. 4.12: Results of the Olympus-InnovX Delta XRF instrument and built-in software. Left image Sb concentrations in Pb-Sb alloys; right image Sn concentrations in Pb-Sb-Sn alloys.

The results for the InnovX α-4000 in Fig. 4.10 show deviations compared to the references up to 8wt% for the Pb-Sb 80-20 wt% alloy. Deviations for Sn were shown to go up to 2.5 wt% for the 80-8-12 alloy. Results for the Niton XL3 instrument in Fig. 4.11 show deviations for Sb up to about 2 wt% for the 80-20 Pb-Sb alloy and also about 2 wt% for the 80-8-12 alloy. The Olympus-InnovX Delta portable XRF results present much smaller deviations for Sb and Sn. The results for Sb are independent of the Sn concentration (Fig. 4.12 Left) and show a maximum deviation of 1.5 wt% for the Pb-Sb 80-20 alloy. For Sn the results deviate slightly with the Sb concentrations (Fig. 4.12 Right), as seen with the other instruments too. The maximum deviation is 0.9 wt% for the 72-16-12 alloy. As opposed to the former two instruments, the results are slightly over-estimated for the Olympus-InnovX Delta software.

The variation in quantifying Sn at different Sb concentrations could be explained by focussing on the Sb-L and Sn-L lines. The spectra present very linear increasing intensity peaks for Sb and Sn. However, it appears that the peak heights (counts) are affected by the concentration of Sb. As an example, the peak height of 12 wt% Sn is lower with an Sb content of 8 wt% (Fig. 4.13 Left) compared to an Sb content of 16 wt% (Fig. 4.13 Right). At a concentration of 8 wt% Sb, the respective peak heights of Sn 4, 8 and 12 wt% are situated at 5300, 9400 and 13600 counts. With a concentration of 16 wt% Sb however, the same Sn concentrations show peak heights at 5500, 10100 and 15000 counts. This effect could be due to secondary fluorescence of Sb on Sn.

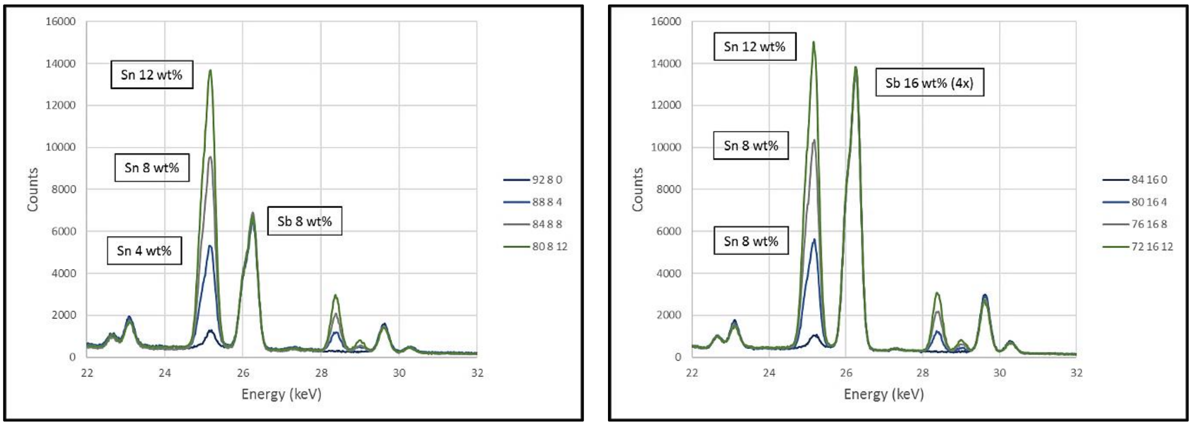


Fig. 4.13: InnovX α-4000 XRF spectrum Sb and Sn-L lines; Left image the intensities of Sn peaks heights with 8 wt% Sb alloys; right image Sn peaks with 16 wt% Sb alloys.

4.3.1.5 Scanning Electron Microscope with Energy-Dispersive X-Ray measurements

Scanning Electron Microscope with Energy-Dispersive X-Ray detector measurements (SEM-EDX) was performed with 20 keV during 100 s live time on alloy bulk areas of c. 600 x 400 µm (Fig. 4.15). The quantitative results obtained with the standard Inca software give deviated results to the alloy compositions (see Fig. 4.14). High Sb and Sn concentrations showed deviations up to 9 and 5 wt% respectively. Several reasons for this can be found, such as the inhomogeneity of the alloys on multi-micron level, the lead rich matrix with a high absorption rate for x-rays and the rareness of these alloys for which the software is not designed. As a consequence, quantification of the SEM-EDX spectra for these kind of alloys should be corrected or the spectra should be quantified by another application, combined with control of the results on external standardised Pb-Sb-Sn alloys.

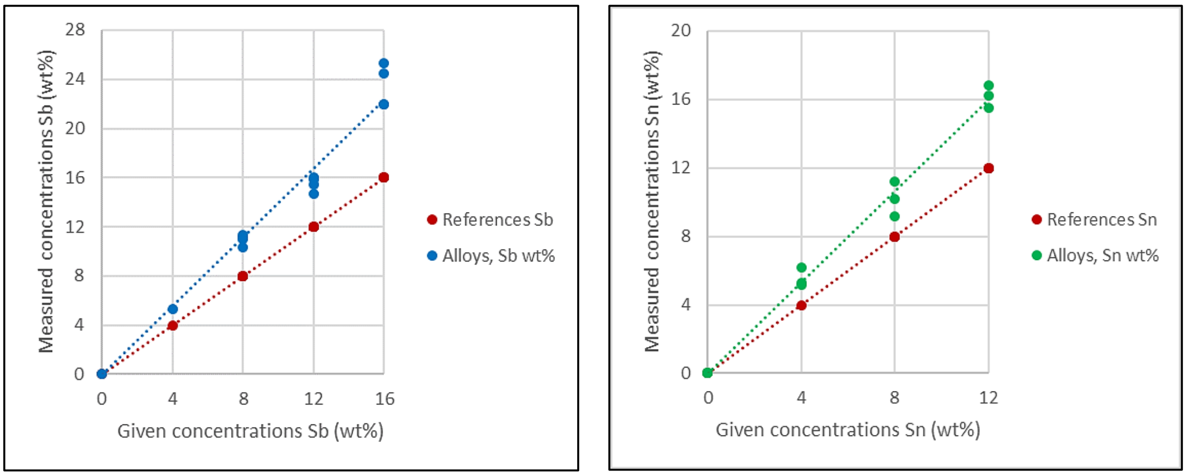


Fig. 4.14: Results of the Quanta 350 SEM-EDX with attached INCA software. Left image Sb concentrations in Pb-Sb alloys; right image Sn concentrations in Pb-Sb-Sn alloys.

Besides the general bulk spectra (Fig. 4.15), distinct alloy phases were investigated in detail (Fig. 4.16). Measurements of a dark phase (SbSn, spectrum 1), a light phase (Pb-rich, spectrum 2) and a eutectic phase (spectrum 3) on alloy 76-12-12 are shown here as an example.

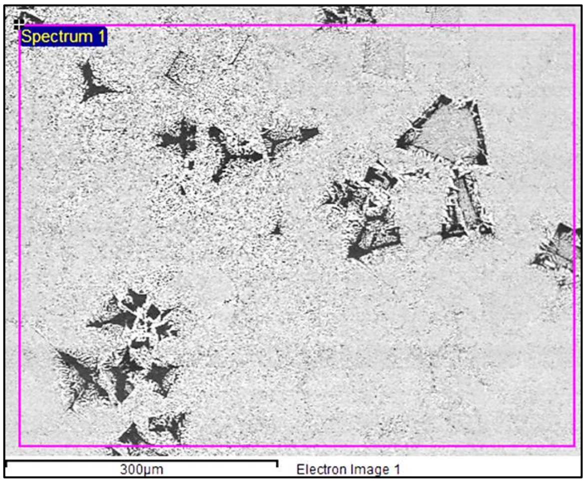


Fig. 4.15: Large area SEM-EDX measurement on alloy ’76-12-12’, approx. 600 x 400 µm (magnification of 500x, scale bar 300 µm).

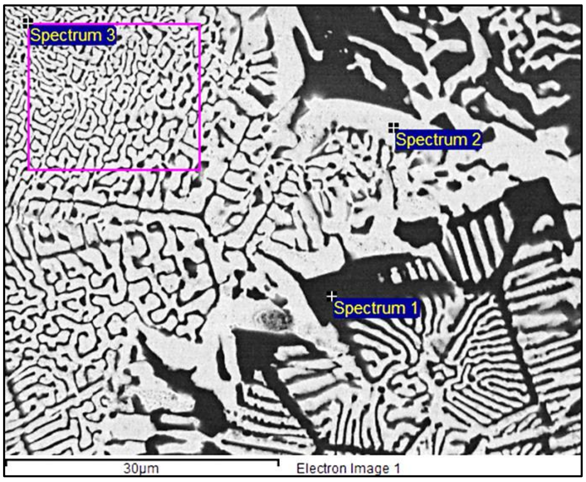


Fig. 4.16: SEM-EDX measurement areas for specific alloy phase areas on alloy ‘76-12-12’ (scale bar 30 µm).

As opposed to the general bulk quantifications where important deviations were predetermined, more precise quantification results can be expected because of the relative homogeneity within each phase area or point of measurement. Consequently, the quotations should be considered as estimates and serve as observations for documenting the differences in microstructure between the produced alloys.

First, the binary Pb-Sb alloys are discussed, followed by the ternary alloys with increasing Sn concentrations at respectively 8, 12 and 16 wt% Sb. For visual comparison, the following images are put side to side. Larger, more detailed images and numeric results are shown in the attachments.

4.3.1.5.1 Binary Pb-Sb alloy phases

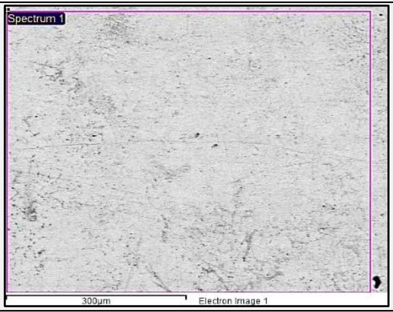
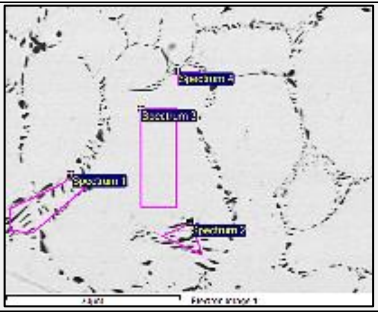
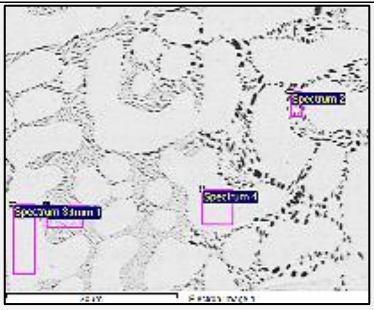
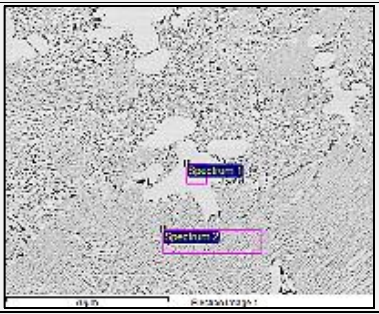
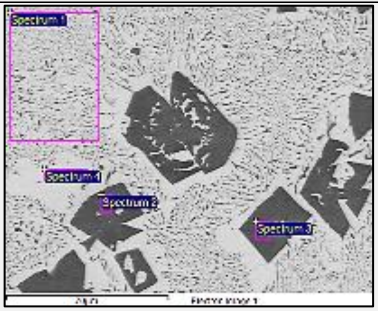
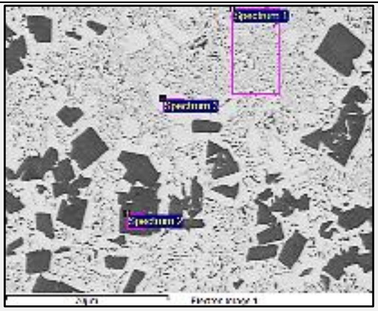
		
100-0-0 (Lead, scale bar 300 µm)	96-4 (scale bar 30 µm)	92-8 (scale bar 30 µm)
		
88-12 (scale bar 70 µm)	84-16 (scale bar 70 µm)	80-20 (scale bar 70 µm)

Fig. 4.17: Series of binary Pb-Sb alloys, showing grain size changes with increasing Sb content and the presence of Sb crystals (black areas) in hyper-eutectic alloy compositions (over 12 wt% Sb).

In pure lead, no microstructure is visible at this scale (600 x 400 µm) because the grains are usually too large and there are no phases to be distinguished with SEM-EDX. When adding 4 wt% Sb, grain boundaries are defined by the segregation of Sb. The Pb-rich grains hold 2 wt% Sb (see Fig. 4.18), while the other 2 wt% Sb segregate as small particles at the grain boundaries. Adding 8 wt% or more Sb to the lead, a maximum dissolution of 4 wt% in the Pb-rich phase is maintained. Starting from 12 wt% addition of Sb, an eutectic structure is visible with an average composition of 16 wt% Sb. Upwards of 16 wt% Sb content, cubic Sb crystals are prominently present.

An observation can be made on the eutectic-like alloys 88-12. Since the true eutectic point is situated at 88.8-11.2 wt% Pb-Sb, alloy 88-12 is in theory hypereutectic and should show Sb segregation instead of Pb-rich phases besides the eutectic phase. However, due to the fast cooling rate of the castings 4 wt% Sb remained dissolved in the Pb-rich grains while the eutectic-like matrix has a composition of 84-16 Pb-Sb wt%. As a consequence, the produced alloys have to be considered as undercooled binary and ternary alloys (Wang, Dai, & Wei, 2007).

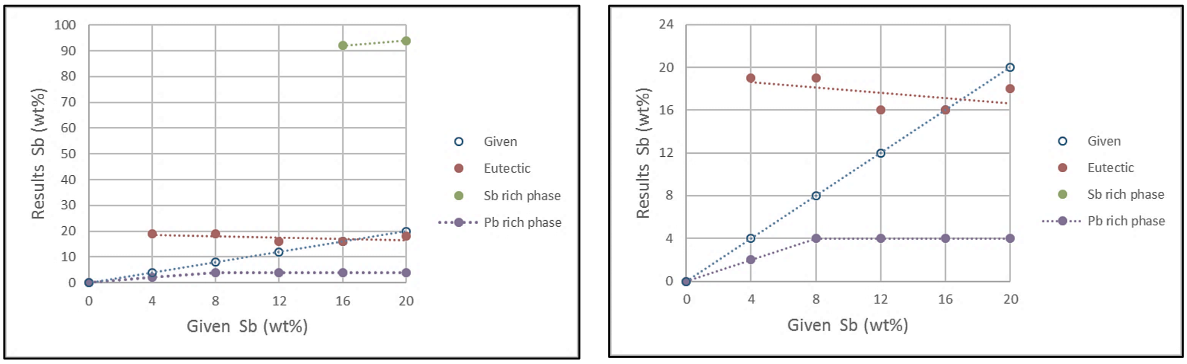
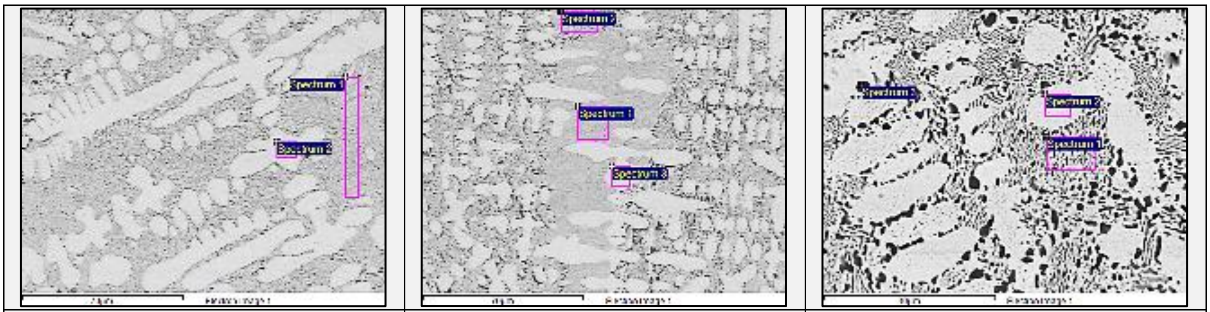
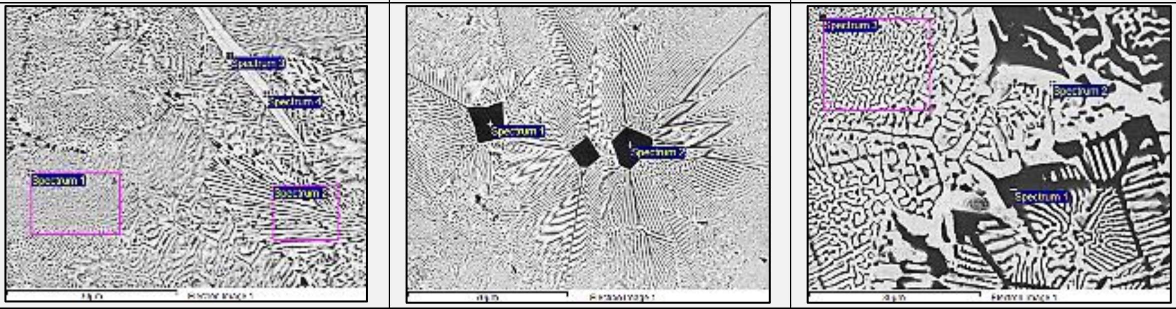


Fig. 4.18: Phase compositions in lead alloys with increasing Sb content. Left: all results including the Sb rich crystals (green dots). Right: detail of the Pb-rich and eutectic phase compositions.

4.3.1.5.2 Ternary Pb-Sb-Sn alloy phases



88-8-4 (scale bar 70 µm) 84-8-8 (scale bar 70 µm) 80-8-12 (scale bar 30 µm)



84-12-4 (scale bar 30 µm) 80-12-8 (scale bar 70 µm) 76-12-12 (scale bar 30 µm)

Fig. 4.19: Series of ternary Pb-Sb-Sn alloys with increasing Sn content (4, 8 and 12 wt%). Upper row: the three alloys with 8 wt% Sb; bottom row the alloys with 12 wt% Sb.

The results for the ternary alloys with 8 wt% Sb and increasing concentrations of Sn show constant levels for Sb in the eutectic and Pb-rich phases with increasing Sn dissolution, respectively at about 15 and 3 wt% (Fig. 4.20). Only with the addition of 12 wt% Sn, is an intermetallic SbSn phase formed with a composition of about 30-40 wt% Sb-Sn.

The results for the 12 wt% Sb alloys with increasing Sn also show drops in levels for Sb in the eutectic but more importantly in the Pb-rich phases (Fig. 4.21). This means that more Sb has been introduced in the SbSn intermetallic phase. The SbSn phase is only present from 8 and 12 wt% Sn concentrations, giving respective composition results of 53-35 and 50-40 wt% Sb-Sn. Nonetheless, there is no result for 80-12-8 because no distinct Pb-rich phase is present in the alloy, most probably because it is so near to the ternary eutectic point (84-12-4 alloy). Particularly with this alloy, a lamellar Pb-rich phase seems to be present together with the Sb-content distributed throughout the eutectic phase.

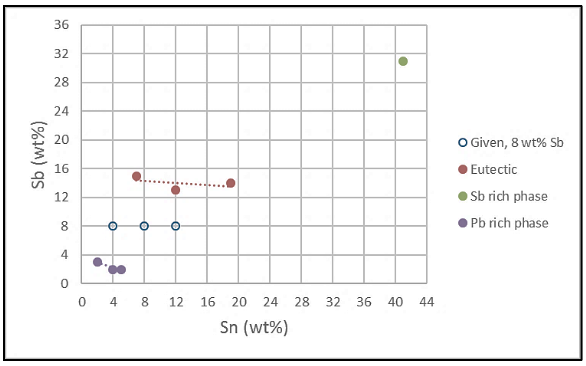


Fig. 4.20: Ternary alloys with 8 wt% Sb and increasing concentrations of Sn (4, 8, 12 wt%).

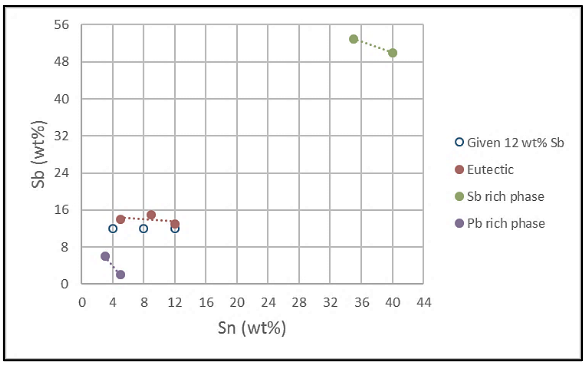
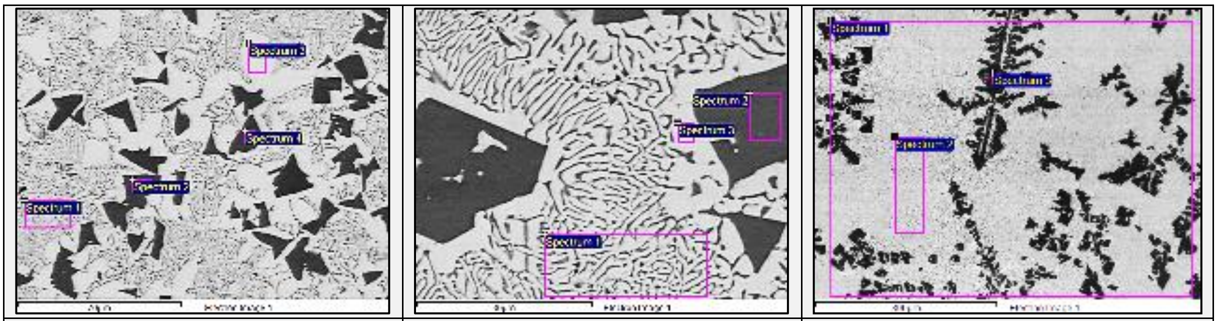


Fig. 4.21: Ternary alloys with 12 wt% Sb and increasing concentrations of Sn (4, 8, 12 wt%).



80-16-4 (scale bar 70 µm) | 76-16-8 (scale bar 30 µm) | 72-16-12 (scale bar 300 µm)

Fig. 4.22: Ternary alloys with 16 wt% Sb and increasing concentrations of Sn (4, 8 and 12 wt%).

The results for the 16 wt% Sb alloys with increasing Sn show a drop in levels for Sb in the eutectic (from 17 to 13 wt% Sb) and constant results at 4 wt% for Sb in the Pb-rich phase, as with the binary Pb-Sb alloys (Fig. 4.23). Only two results for Pb-rich phases were obtained since this phase does not appear with the 76-16-12 alloy, showing only eutectic and Sb-rich phases. Concerning the Sb-rich phase, at 4 wt% Sn the SbSn crystals have a composition of 83-13 wt% Sb-Sn, dropping to an average of 53-33 wt% Sb-Sn for the 8 and 12 wt% Sn concentration respectively.

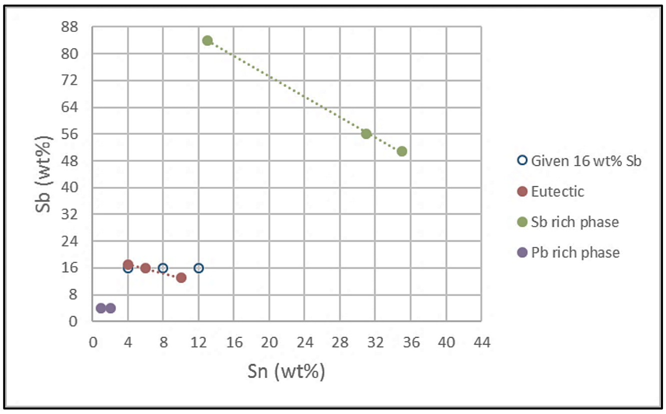


Fig. 4.23: Ternary alloys with 16 wt% Sb at increasing concentrations of Sn (4, 8 and 12 wt%).

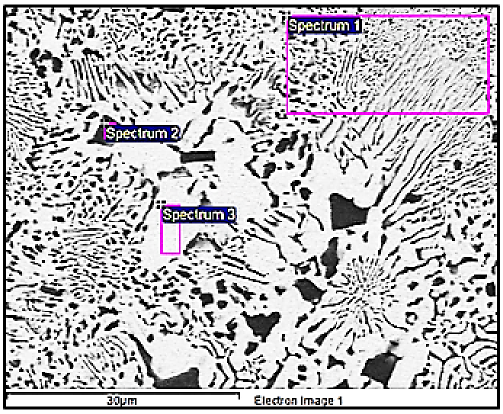


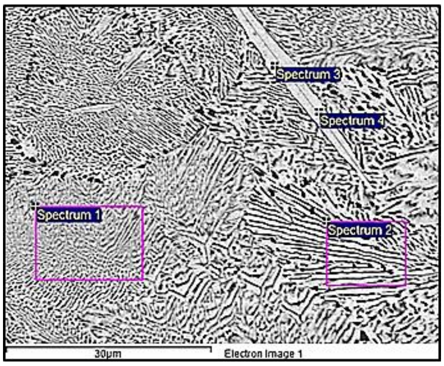
Fig. 4.24: The pseudo-eutectic alloys of 80-10-10 wt% (scale bar 30 µm).

The results of the pseudo-eutectic phase alloy 80-10-10 (Fig. 4.24) give an overall composition of 76-12-12 wt%, a Pb-rich phase (spectrum 3) of 94-2-4 wt% and an SbSn phases of resp. 12:11 Sb:Sn in spectrum 1 and 47:38 Sb:Sn in spectrum 2; all results fit within the previous measurements.

4.3.1.6 Conclusions on the microstructures and chemical-physical measurements

ICP-OES measurements have shown that the respective compositions of the produced alloys are sufficiently precise to be used as references within the scope of this research.

Hardness values, as shown in Fig. 4.7 and Fig. 4.9 indicate higher numbers for increasing levels of Sb and Sn, although the rise is not linear with the concentrations. This might be due to the phase formations and their distribution throughout the alloy. Although the eutectic and the Pb-rich phases are relatively consistent in their Pb-Sb-concentration with changing Sn content, the hardness, form, size and distribution of the Sb-rich phases is particular for each of the examined alloys.



Considering the type metals that were used in the 16th century, when printers were searching for the best (i.e. hardest and finest casting) alloys at the lowest possible cost, it seems that within the range of the examined alloys, 84-12-4 would have been an optimum. It gives a Vickers hardness of 23 while the least expensive Sn is needed. One hypothesis for this result is the specific microstructure of this alloy, showing lamellar Pb-rich phases in a high-Sb containing eutectic (Fig. 4.19, copy image on the left).

XRF can be considered a valid method for quantifying lead alloys, when appropriate reference material is used for the correction of the numeric results obtained from the instrument. The use of different software to quantify peak intensities could be more suitable for quantification; however, for conservation where large numbers of items often have to be checked, the use of straight available data is beneficial. Moreover, peak intensities for Sn seem to be variable with the Sb content in the Pb-rich matrix. This would result in a fluorescence effect, which means that linear corrections for Sn without taking Sb into account are not applicable. For the three instruments and their software used, a continuous under-estimation for Sb and Sn was reported. The Olympus-InnovX Delta Professional with built-in software did however perform very well, with numeric results that lie within 1% error margins for alloys up to 16 wt% Sb and 12 wt% Sn. The alloy Pb-Sb 80-20 wt% gives an overestimation of about 1.5 wt% for Sb. All following XRF measurement results are denoted ‘XRF’ and were collected using the Olympus-InnovX Delta professional instrument.

SEM-EDX measurements with the standard settings of the INCA software, even if calibrated with external units for the measured elements, are not close to the actual ratios when measuring the alloys in bulk. This is due to the inhomogeneity of the phases and their distribution in the Pb-rich matrix. In contrast to XRF, a continuous over-estimation for the Sb and Sn values was recorded. It is therefore required to check and correct the settings in the INCA software using a standardised set of Pb-Sb-Sn alloys when needed. Measuring individual phases however seem to give more precise composition ratios, since the negative effect of other phases present and inhomogeneity are surpassed.

Studying the microstructures and the phase compositions shows the complexity and the large variation between all the produced alloys. Furthermore, the results show that these alloys must be considered as undercooled microstructures. This may have an effect on precise values for hardness, but plays no role in the quantitative measurements of the alloy compositions.

4.3.2 Historical type

4.3.2.1 Selection 1: Types from c. 1553-1825

The types were cleaned of corrosion on one side, giving access to the bulk composition for the measurements. The results of XRF measurements are presented in Table 4.5. In this table, the typeface, the author (punch cutter) and the year (approximate) of cutting or production is noted. The addition 'Confirmed' (C) points to archival documents where the cast type has been delivered to Plantin, namely 18th and 19th century items. These type pieces are important in the MPM collection since no punches or matrices were ever at the Plantin and Moretus print shops. In this respect, the lead types are the only surviving materials representing these typefaces in the MPM collection and must be considered very valuable for this reason.

Table 4.5: XRF results on types from Selection 1. Element concentrations in wt%. Abbreviations –o and b are respectively 'onderkast' (lower case) and 'bovenkast' (capitals).

Inv. N°	Typeface	Author	Year	Pb	Sb	Sn	Other
IT 4-o	Parangon	Granjon	v. 1554	81.0 (±0.8)	16.4 (±1.7)	2.5 (±2.2)	
IT 6-o	Philosophie	J. Gillé	v. 1766 (C)	79.0 (±3.2)	20.6 (±2.9)	0.4 (±0.7)	
IT 9-o	Text	Gando	c. 1825 (C)	83.3 (±2.2)	16.1 (±1.4)	0.6 (±0.8)	
R 6-o	Mediaan	Hartung	v. 1821 (C)	76.0 (±2.7)	22.9 (±3.0)	1.1 (±0.6)	Cu 0.1
R 7-b	2 R Brevier	Fournier	1742 (C)	76.8 (±1.7)	20.7 (±1.3)	2.5 (±0.4)	
R 31-o	Brevier	Hartung	v. 1821 (C)	80.3 (±0.7)	19.4 (±0.4)	0.3 (±0.3)	
R 39-o	Brevier	Hartung	v. 1821 (C)	81.4 (±2.0)	18.5 (±1.9)	0.1 (±0.1)	
R 54	Canon	Gando	c. 1825 (C)	79.6 (±1.6)	19.5 (±1.7)	0.8 (±0.2)	Cu 0.1
R 55	2 R Augustijn	Fournier	1742 (C)	77.8 (±0.6)	19.5 (±0.6)	2.7 (±0.1)	
R 56	Klein Canon	J. Gillé	v. 1766 (C)	78.1 (±1.4)	21.2 (±1.5)	0.7 (±0.1)	
R 65	Groot Canon	V d Keere	v. 1570	77.8 (±1.0)	18.5 (±0.9)	3.7 (±0.1)	Cu 0.1
R 89-o	Augustijn	Voskens	c. 1705 (C)	78.3 (±0.9)	20.2 (±1.5)	1.5 (±0.7)	
R 129-o	Brevier on Coronelle	Garamont	v. 1553	76.6 (±2.0)	21.8 (±3.2)	1.6 (±1.3)	
R 129-b				77.4 (±2.3)	21.7 (±2.7)	0.9 (±0.4)	
R 131-o	Brevier	Garamont	v. 1553	75.9 (±1.5)	22.8 (±2.2)	1.2 (±1.0)	
R 136-o	Nonpareille	Haultin	v. 1553	72.9 (±2.0)	25.8 (±2.6)	1.3 (±1.0)	
R 136-b				78.2 (±1.3)	19.8 (±1.9)	1.9 (±0.6)	
R 142-o	Nonpareille	Haultin	v. 1553	77.6 (±1.6)	16.5 (±0.8)	5.8 (±2.0)	Cu 0.1
T 3-o	Parangon	V d Keere	1570	75.8 (±6.4)	17.9 (±3.3)	6.2 (±3.2)	

The analytical results for all measured types are relatively close to each other, i.e. Pb 78.1 wt% (±2.4), Sb 20.0 wt% (±2.5) and low tin contents of 1.9 wt% (±1.7). The standard deviation for the Sn concentrations is rather high because of a few sets that show higher values, i.e. R 142-o and T 3-o with respectively 5.8 and 6.2 wt% Sn. The types confirmed by archival documents (C) were cast in the 18th and 19th centuries. The averaged compositions of the exclusively confirmed sets are Pb 79.1 wt% (±2.2), Sb 19.9 wt% (±1.8) and Sn 1.1 wt% (±0.9).If these compositions were to be extrapolated for the 18th and 19th centuries, it would mean that this kind of composition for lead types could be considered a standard at the Plantin printshop: Pb 79, Sb 20 and Sn 1 wt%.

However, the compositions of the other non-confirmed sets lie very close to the averaged values of the confirmed sets and could well have been cast in these later periods as well. Only R 142-o and T 3-o hold somewhat higher values for Sn, making them a possible exception to this hypothesis, perhaps dating from an earlier period.

4.3.2.2 Selection 2: 16th-17th centuries type pieces

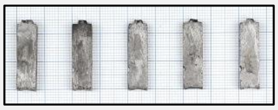
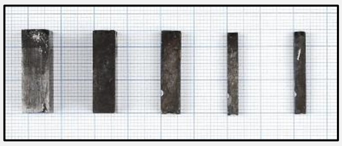
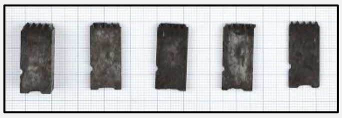
The selection of the type pieces, all attributed to 16th century cutters in style, was based on the assumption that some of them were no longer used from the beginning of the 17th century (i.e. Ethiopean 'ET' and Hebrew 'H') while Fleuron ('FL') were in use for a longer period of time, as was the music type ('MU'). However, no exact time slots can be defined without extensive research into the books that were printed with these characters.

This selection of types, as specified by its inventory listing (see Table 4.2), results in metal concentrations listed in Table 4.6. Only the type from sets MU 3 and MU 6, attributed to Van den Keere, show relatively large deviations for the antimony and tin contents. Together with FL 3-1,2, also attributed to Van den Keere, they have very low tin concentrations. Even though Van den Keere also delivered cast type, these types may have been cast in a later period. In this respect, another observation has been made on FL3-2, which has been finished with extreme accuracy just like FL3-1, but shows radial lines of a planing machine with such an accuracy that it has to be estimated at least as a 19th century finish. According to this, the alloy containing a high amount of antimony and a low tin concentration is coherent. A similar conclusion could be drawn from MU 3 and MU 6, which might be later recasts as these music types were used well into the 17th century. The matrices for these faces also still appeared in the Octavo Inventory of 1652 [Arch. 154, p.1-9]. Group MU 9 however shows a much higher tin content, together with an elevated copper presence.

High to extremely high concentrations of tin and copper and low concentrations of antimony are found in groups H 2 and FL 3-4,5, both attributed to Granjon (Vervliet, 2015). Special attention can be focused upon these last two type pieces. There are no punches in the Plantinian collection and the matrices were traded or lost at some point in time. As neither Granjon nor Plantin cast lead type themselves, it is possible that these lead types were acquired from a typecaster and may date originally from the 16th or 17th century. The medium high amount of tin and the low antimony concentrations support this idea.

The variations in composition of the type, even from similar periods in time, are to be explained by several factors, such as remelting of older type with imprecise known composition, the renewal of the melting pot content during large casting sessions and the freedom of the caster to adapt the composition (e.g. by adding tin for a sharper cast of small type).

Table 4.6: XRF results for the metals, present in the measured alloy (expressed as wt%).
Types items (i.e. ET 1) are on the photos to be read from left to right (i.e. ET 1-1 to ET 1-5).

	Sample	Cutter	Pb	Sb	Sn	Cu	Fe
	ET 1-1	Unknown (Hand B)	87.6	4.3	7.8	0.1	0.1
	ET 1-2		86.7	4.4	8.7	0.1	0.1
	ET 1-3		89.0	3.8	7.0	0.2	0.0
	ET 1-4		86.5	4.5	8.8	0.2	0.1
	ET 1-5		86.9	4.3	8.5	0.1	0.0
	H 2-1	Unknown	77.2	3.4	19.1	0.2	0.1
	H 2-2		77.3	3.9	18.3	0.4	0.1
	FL 3-1	H. van den Keere	82.3	15.8	1.6	0.1	0.1
	FL 3-2		82.1	16.0	1.4	0.1	0.1
	FL 3-3	Granjon	86.0	4.3	8.8	0.2	0.2
	FL 3-4	Granjon	83.8	3.2	12.5	0.3	0.1
	FL 3-5		84.4	3.0	12.1	0.2	0.2
	MU 3-1	H. van den Keere	85.7	12.3	1.1	0.1	0.1
	MU 3-2		90.3	7.1	2.3	0.1	0.1
	MU 3-3		89.8	7.3	2.4	0.1	0.1
	MU 3-4		85.1	12.6	1.8	0.1	0.1
	MU 3-5		87.8	9.9	2.1	0.1	0.0
	MU 6-1	H. van den Keere	91.7	5.5	2.6	0.2	0.1
	MU 6-2		89.2	7.8	2.6	0.1	0.1
	MU 6-3		89.3	7.2	3.3	0.1	0.1
	MU 6-4		91.5	5.7	2.5	0.2	0.0
	MU 6-5		89.7	7.6	2.4	0.2	0.1
	MU 9-1	H. van den Keere	84.5	6.0	9.1	0.2	0.1
	MU 9-2		82.0	5.3	12.2	0.2	0.1
	MU 9-3		84.6	5.0	10.1	0.2	0.1
	MU 9-4		83.5	4.7	11.5	0.3	0.1
	MU 9-5		85.6	4.6	9.3	0.2	0.1

4.3.2.3 Selection 3

4.3.2.3.1 Hebrew (Inv. N° MPM.V.V.2.6.H.001-002), Syriaque, Samaritain and Ethiopean types.

The cases with these types are on exhibition in the print room. They hold ‘Lage Text Hebreeuws op Text en Augustijn’ for n° 001 and 5 Hebrew polis for n° 002, both attributed to Guillaume Le Bé (I). The latter is a collection of types ‘lage Double Parangonne Hebreu’ (16 types), ‘lage Double Augustine Hebreu’ (43 types), ‘lage Kleine Text Hebreeuws op Text, Augustijn en Colineus’ (36 types), ‘lage Coronelle Hebreeuws’ (30 types) and ‘lage Augustine vieille Hebreu op Augustijn en Philosophie’ (57 types).

Fig. 4.25: Left: the Hebrew type on display in the museum in the distribution trays, covered by glass for protection from the visitors. Right: detail of the compartments, which are lined with heavy paper.

From these types, each of the characters was selected to compose standing types in order to print so-called ‘type specimens’. In other words, for each kind of font, an alphabet was composed to print a representative page (Fig. 4.26). All Hebrew types are denoted as H 1, H 2, until H 8. Both ‘Syriaque’ are SY 1 and SY 2, ‘Samaritain’ SA 1 and ‘Ethiopean’ ET 1. These sets of types are regarded to be the oldest types in the MPM, dating from the 16th or the very early 17th century. The argument is that the Moretusses did not print, or very rarely printed, Hebrew after 1606 (Imhof, 2014). From each set (H 1, H 2, etc.), the first 10 types were selected to perform the analytical measurements on (see Fig. 4.26). The other types are illustrated in the attachments.

Fig. 4.26: Example of the type specimen H III (Hebrew 2 regelen Mediaan, Le Bé), with the first 10 characters selected, on which the analytical measurements were performed (red frame).

The measurement results are presented in Table 4.7. The selection of types from the sets H 4, H 5, SA 1 and ET 1 gave closely matching results for the 10 measured pieces. However, the majority do not show homogeneous results and the groups with similar compositions are denoted in Table 4.7 with the respective number of pieces. Single pieces with deviated results are excluded from this table.

Table 4.7: XRF results on the compositions of the Hebrew, Syriaque, Samaritain and Ethiopean types. Grouping of the alloy compositions is denoted as amount to a total of 10 (#/10).

N°	Description	#/10	Cutter or period attributed	Composition in wt%			
				Pb	Sb	Sn	Cu
H 1	Double Parangon Hebreu	9	Le Bé, 1559-1570	69.7 (±2.3)	5.2 (±0.4)	24.2 (±1.7)	0.5 (±0.23)
H 2	Double Augustin Hebreu	4	1523	81.3 (±0.3)	9.2 (±0.2)	8.9 (±0.2)	0.4 (±0.22)
		3		78.5 (±0.4)	10.7 (±0.3)	10.0 (±0.2)	0.5 (±0.12)
H 3	2 Règles Mediaan (Hebreu)	3	Le Bé, 1559-1570	77.4 (±0.7)	1.8 (±0.5)	19.5 (±1.4)	0.4 (±0.11)
		3		79.2 (±0.9)	7.9 (±0.4)	12.1 (±1.0)	0.2 (±0.06)
		2		85.0 (±0.9)	5.6 (±1.1)	8.7 (±0.0)	0.1 (±0.01)
		2		62.3 (±0.3)	0.6 (±0.1)	36.2 (±0.3)	0.3 (±0.01)
H 4	Text	10	Le Bé, 1559-1570	72.4 (±1.2)	4.3 (±0.4)	22.6 (±1.1)	0.4 (±0.09)
H 5	Kleine Text	10	1517	72.9 (±3.2)	6.4 (±1.0)	19.7 (±3.2)	0.4 (±0.16)
H 6	Augustine vieille Hebreu	6	1564	70.7 (±0.8)	5.0 (±0.1)	23.6 (±0.7)	0.4 (±0.05)
		3		77.3 (±0.8)	6.5 (±0.5)	15.6 (±0.2)	0.3 (±0.04)
H 7	Hebreu sur petite Augustine	5	1517	70.2 (±2.2)	5.6 (±0.2)	23.6 (±2.2)	0.3 (±0.15)
		3		74.8 (±0.1)	5.7 (±0.0)	18.9 (±0.0)	0.3 (±0.08)
		2		81.3 (±1.3)	5.9 (±0.5)	12.1 (±1.0)	0.1 (±0.01)
H 8	Coronelle	6	Le Bé, 1559-1570	66.7 (±2.2)	7.6 (±0.5)	24.0 (±1.9)	0.7 (±0.17)
		3		87.0 (±149)	11.7 (±1.1)	0.1 (±0.2)	0.3 (±0.07)
SY1	Augustijn	7	Granjon 1570	80.3 (±1.8)	4.0 (±0.6)	14.9 (±1.3)	0.4 (±0.15)
		3		72.2 (±1.5)	1.7 (±0.9)	25.4 (±1.9)	0.4 (±0.08)
SY2	Augustijn Estrangelo	8	Granjon 1570	82.1 (±1.2)	4.0 (±0.3)	13.3 (±1.0)	0.3 (±0.07)
SA1	Mediaan	10	End of 16th C	83.9 (±1.1)	5.4 (±0.3)	10.3 (±0.9)	0.2 (±0.05)
ET1	Mediaan	10	End of 16th C	84.7 (±0.8)	5.2 (±0.2)	9.8 (±0.6)	0.1 (±0.02)

Two observations can be made from the results. First, a large variation in concentrations of antimony and tin is present across the fonts. The most tin-rich lead alloy is found with 2 Règles Mediaan (Hebrew, Le Bé), giving a concentration of over 36 wt% tin, whereas antimony is less than 1 wt%. All others (except for 3 types from H 8) show tin concentrations between 8.7 and 25.4 wt%. The antimony concentrations in these alloys vary between 0.6 and 11.7 wt%. The three types from H 8 with almost no tin (above) show 11.7 wt% antimony (Fig. 4.27).

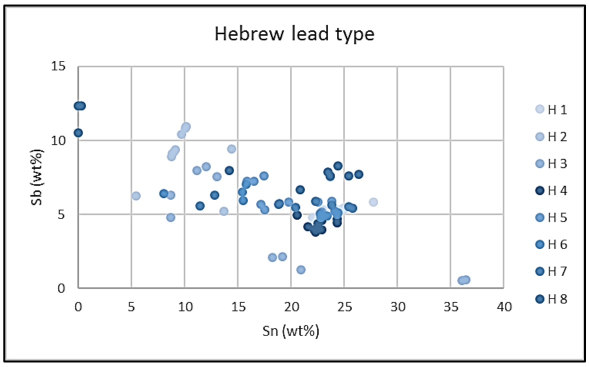


Fig. 4.27: XRF results for Sb and Sn on the compositions of the 8 Hebrew types.

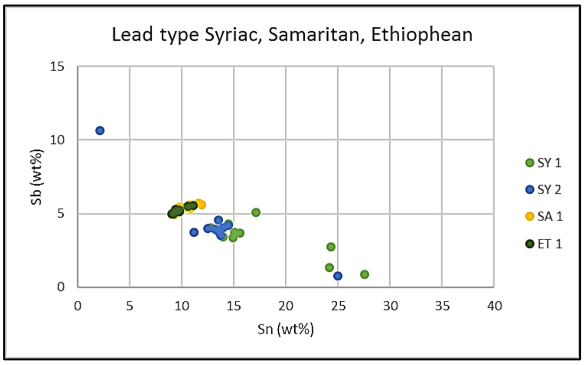


Fig. 4.28: XRF results on type sets SA 1 - ET 1 and SY 1 - SY 2, Sb and Sn concentrations.

The sets SA 1 and ET 1 are striking in that they not only show homogeneous results throughout the 10 measured pieces (Fig. 4.28), but also seem to be very close to each other in compositional results (i.e. c. 10 wt% Sn and 5 wt% Sb). They are both attributed by Carter to the end of the 16th century. SY 1 and SY 2 are relatively closely grouped too, with an average of 13 wt% Sn and 4 wt% Sb, but both also show some types with equally deviating compositions.

4.3.2.3.2 Initials 'Cadeau' with grotesks (Inv. N° MPM.HB.13567, 13582, 13584, 13763, 13764)

The large format initials (c. 50 x 50 mm) are lead cast wafers of about 3 mm thickness, fixed on oak wood bases. They are dated to 1575 and exist as a pool of 18 pieces (nos. 13567-13584), not attributed.

Fig. 4.29: Fronts, sides and backsides of the 5 measured printing blocks. While some are covered with paper at the back, others are free of paper and show the two drilled holes in the wood, which are filled with molten metal.

Particular in this case are the metal pins which appear to be cast into holes in the wood (Fig. 4.29 and Fig. 4.31). They hold the print faces in place on the wooden body. Measurements on the faces and on the pins are presented in 4.3.2.3.8.

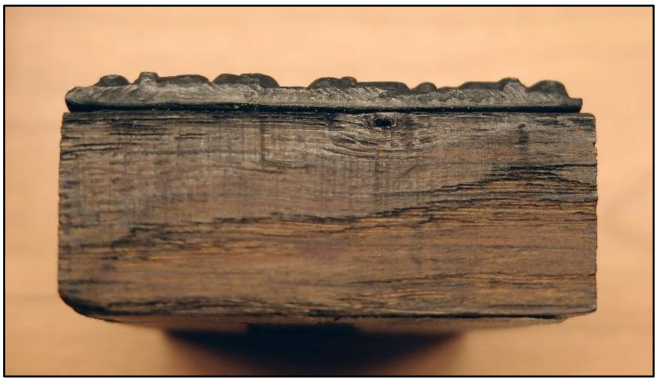


Fig. 4.30: Side of the printing block showing the thin wafer of cast lead alloy on top of the oak base.

Fig. 4.31: Detail of the two holes filled with a low melting lead-tin alloy.

The faces of these types show the following composition: Pb 79.8 wt% (±2.9), No Sb and Sn 18.1 wt% (±2.6). The high Sn content and virtual absence of Sb is remarkable. Two measurements on the pins at the back of the wood show the following: Pb 51.5 wt% (±7.8), No Sb and Sn 47.1 wt% (±7.8). Such a composition is considered to be a solder. For its purpose here, the low melting point enables the bonding with the back of the faces, whilst pouring the molten composition through the holes from the back of the wooden support (see low melting point and alloy specifications, phase diagram Pb-Sn in Chapter 1).

4.3.2.3.3 Wooden type that was copied in metal (MPM.ST.001[4], Lead MPM.V.V.02.6.R.148)

Description of this type reads '*La Plus Grande Romaine, Hendrik van den Keere, finished in April 1575 but probably started some time earlier, a roman of heavy weight and cut in wood and cast in sand, possibly the original Dutch method for casting movable types. Plantin used it for folio title pages, posters and placards*' (Parker & Melis, 1960). In the MPM collection, 73 wooden forms are preserved.

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[4] Lists at the MPM sometimes refer to a certain set, for instance ST.001, ST.003, etc., or ST 1, ST 3, etc.; the reader should consider them the same.

Early large character types were often cut in wood, to print directly or to be copied in lead by means of sand casting. Although this is the usual method found in historic literature and as described by recent historians, from a metalworker's point of view it is equally possible to copy them using the lost wax method for casting in more durable alloys. It is possible to make an imprint in another material such as plaster to obtain a negative form. In this, wax is applied to obtain a positive again. This wax model can be embedded in clay, which is left to dry and is heated until the wax form runs out. In the cavity that remains, a metal alloy could be cast. This may have been bronze, brass, tin or a lead alloy. Perhaps this is what Sabon claimed to do as described in the Frankfurter privileges (Meldau, 1935) with the use of copper alloys for the production of type.

Fig. 4.32: Box with the wooden type models, capital letters and lower case letters.

Fig. 4.33: Detail of the letter E.

For the lead casts of these types (Fig. 4.34), van den Keere charged Plantin on April 16th 1575 for 6 florins '*pour le pourtraict de la reste de la grosse Romaine molee / et ce que Jay payé au menuysier pour les separere et acconstrer avec la fonte en sablon et la iustification des lettres fondues pour les mots suyvants Psalterium dispositum per hebdomadum.*' [Arch. 153 p.160; 42, p.3v°]. In later inventories there are several descriptions of similar type, which was delivered by van den Keere to Plantin, although it remains uncertain if it concerns exactly these type pieces that still remain in the museum. In any case, the type surviving at the museum indicates that the letter was cast in sand as only a thin wafer of lead, justified and cast in a mould to form the shank. (Fig. 4.35)

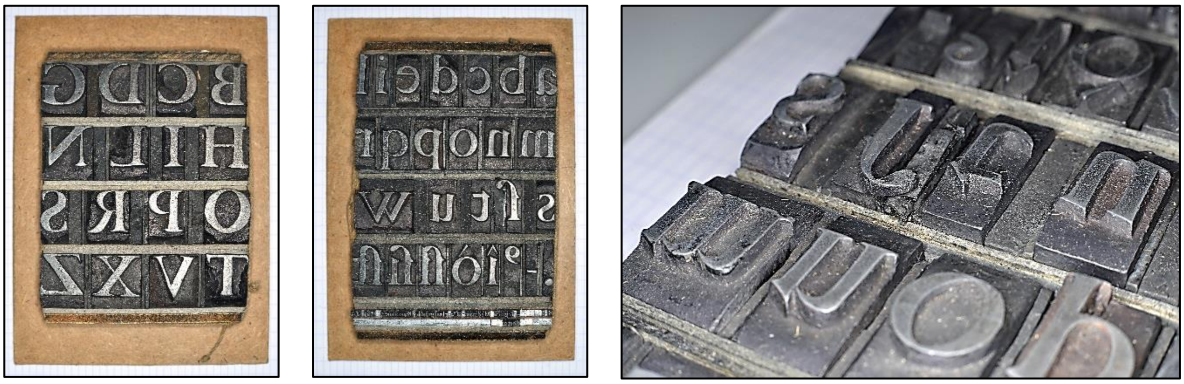

Fig. 4.34: Lead type cast from the wooden models above. The standing type composition with solitaire letters are respectively 12 x 15 and 12 x 17 cm large. The right image is a close-up.

Fig. 4.35: Details of the sides show that the body was cast upon the face, which has an average thickness of about 4 mm.

Measurements on the faces and on the shanks show non-homogeneous results, divided into three groups for the faces of the types as 3 different groups for the shanks (Table 4.8 and Fig. 4.36). For the lower case types (Fig. 4.37), homogeneous results are recorded except for the shank of ‘e’ with a deviant composition: Pb 72.1 wt%, Sb 2.1 wt% and Sn 24.6 wt%.

Table 4.8: XRF measurements results on the lead type ST 1, faces and shanks.

Description	Glyphs	Composition in wt%			
		Pb	Sb	Sn	Cu
Faces, group 1	B I T V	79.9 (±0.8)	6.8 (±0.2)	11.9 (±0.9)	0.2 (±0.05)
Faces, group 2	G H L O R Z	85.6 (±1.0)	3.3 (±0.3)	10.0 (±0.6)	0.2 (±0.02)
Faces, group 3	C D N P S X	83.1 (±1.0)	6.8 (±0.5)	8.9 (±0.5)	0.2 (±0.13)
Shanks, group 1	B O Z	88.8 (±0.8)	2.7 (±0.1)	7.4 (±0.3)	0.1 (±0.01)
Shanks, group 2	G H L	93.0 (±1.2)	2.2 (±0.1)	3.8 (±0.6)	0.1 (±0.00)
Shanks, group 3	C D I N P S T V X	82.5 (±0.9)	6.7 (±0.7)	9.8 (±0.7)	0.2 (±0.03)
Lower case, Faces	All	85.0 (±2.5)	6.2 (±0.9)	7.4 (±1.9)	0.3 (±0.10)
Lower case, Shanks	All, except ‘e’	87.1 (±1.7)	5.9 (±0.7)	6.4 (±1.2)	0.2 (±0.07)

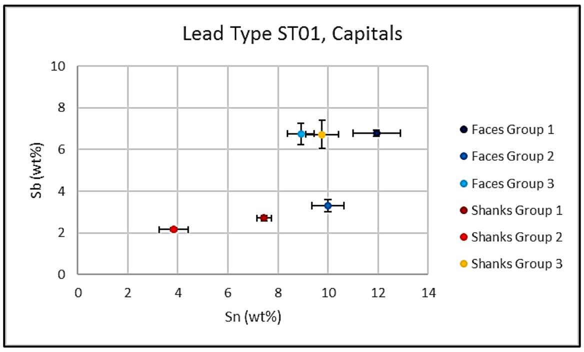

Fig. 4.36: XRF results for the capital letters, faces and shanks of the groups, as indicated in Table 4.8.

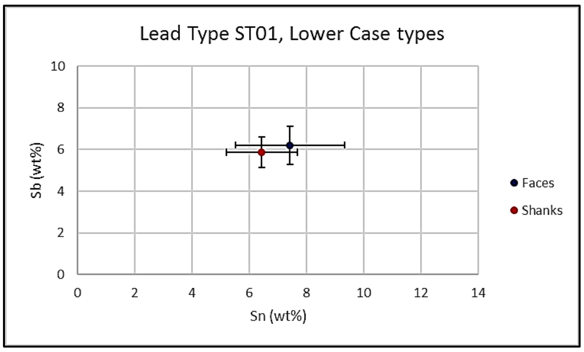

Fig. 4.37: XRF results of the lower case type pieces on the faces and on the shanks.

4.3.2.3.4 Grosses Capitales Extraordinaires (MPM.ST.003)

The punches for this typeface were left unfinished by Claude Garamond in 1561. The Romans were finished by Jacques Sabon in 1565 and the Greek by Hendrik van den Keere in 1570. There are 38 punches in total, of which 34 are from Garamond's hand; the punch for 'C' is unlike the rest in shape and finish. It was cut by Hendrik van den Keere in 1570, as a bill to Plantin states: '*la taille de 11 poinsons des grosses Capitales Grecques et le C des Romaines / recue et Retrempe le B.K.Q.I. et* autres' (Parker & Melis, 1960). For this face, there are two sets of matrices in the MPM: MA 78 (Parker, Melis, & Vervliet, 1960) and MA 9 (lacking the 'O') (Parker, Melis, & Vervliet, 1960). Set MA 78 is described as 'brass' matrices, but consists mainly of copper pieces, except for the AE and W that are in brass but which are most probably later additions (see Appendix). Set MA 9 was probably produced by Sabon while he worked in Antwerp. Both sets have the 'C' of van den Keere, which he probably added to MA 78 in late 1570 (when he had cut the punch for 'C') or very early in 1571 when he billed Plantin in January for 'a strike of the capitals on which he was working' (Parker & Melis, 1960). (For the matrices' compositions: see Chapter 5)


Fig. 4.38: Showcase with lead types from ST 3.


Fig. 4.39: Standing type composition.


Fig. 4.40: The complete set of steel punches, ST 3.


Fig. 4.41: Compartment of the exhibition case for the types 'C', cast on a high corpus.


Fig. 4.42: Compartment of the tray V.V.2.6.R64, on an x-height fitting corpus.

Besides the punches and the matrices, there is also lead type preserved for this face. The inventory numbers in the MPM are respectively MPM.V.V.02.6.R.013.o, -b and –R.064. There is also standing type present, which was composed between 1985 and 1996. Peculiar to this set of lead type is the existence of the capital 'C' with serifs, which would be from Garamond's hand, or perhaps from Sabon's hand finishing the Romans. An original fount may also have been cast by Sabon while he worked for

Plantin.[5] Since the steel punch that is here now was cut by van den Keere (different from the rest of the set of punches), and the copper and the lead matrices all have a 'C' without serifs, there is no certainty that the lead type of this fount with the 'C' without serifs, is from the 16th century. In Fig. 4.43 to Fig. 4.46, the steel punch for this 'C', a lead matrix from MA 9, a copper matrix from set MA 78 and a lead type are shown. The original marks from the counterpunch in the centre of the steel punch 'C' were copied into the copper matrix and subsequently into the lead cast type.

Fig. 4.43: Punch for C ST3, mirror image.

Fig. 4.44: C of the lead matrices, set MA 9.

Fig. 4.45: C as matrix from set MA 78.

Fig. 4.46: Lead type, mirror image.

Chemical analyses performed in 1963 on a lead type of a C with serifs[6] revealed 82.3% Pb, 10.0% Sn, 5.9% Sb and 0.1% Cu. This specific type piece was not available at the time of this study, therefore no comparative measurement could be made; however, this composition fits within the range of alloys measured throughout the exhibited fount of these types (MPM.V.V.02.6.R.013). In Fig. 4.47 a comparison shows the different widths (identical blue boxes on each glyph) of the two types of 'C'. It is not only the serifs that make the early 'Sabon'-C different; it is also more narrow compared to Van den Keere's C without serifs.

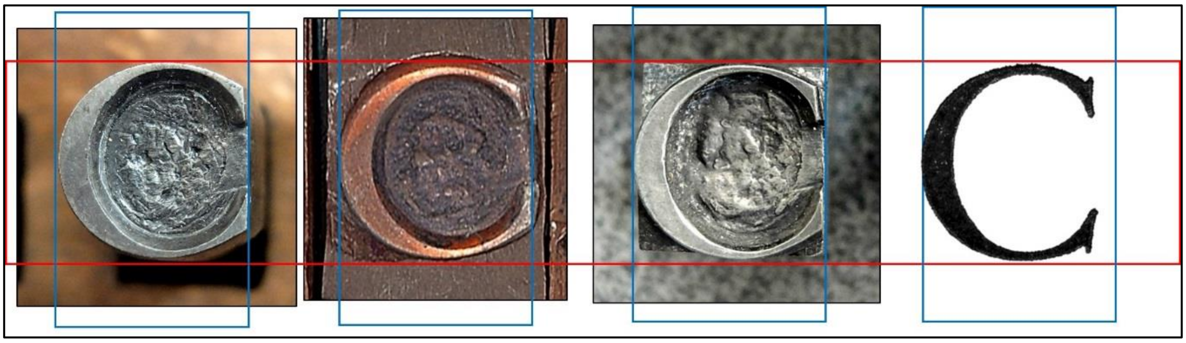

Fig. 4.47: Comparison of the widths of the C without serifs (first three from the left, being punch, matrix and type) and with serifs (far right) on identical x-heights (red box).

The analytical results show compositions with varying amounts of tin and antimony (see Fig. 4.48). Measurements for each character were executed on the face and on the shank, giving similar results (two types of 'C' were measured and averaged together). The total average of all results is a composition of Pb 82.4 wt% (±4.3), Sb 5.9 wt% (±2.5), Sn 11.5 wt% (±3.4) and Cu 0.3 wt% (±0.2),

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[5] Sabon worked with Plantin from 1565 and a letter from Prof. Vervliet to H. Carter on 12 June 1963 mentions the 'early serifed C which was made by J. Sabon in 1566 and was replaced in 1570 by a C by H. Van den Keere'.

[6] Cfr. Letter from Vervliet to Carter and the analysis results from the Royal Institute for Cultural Heritage in Brussels, dating 7 June 1963.

although it should be noted that only 2 major groups (Groups 1 and 2 in Fig. 4.48) are to be distinguished, besides a number of different compositions that were apparently used (see Table 4.9). The two major groups of respectively 11 and 10 pieces consist of a random selection of Roman and Greek characters. Other types vary in composition. The 'J' and 'U' are of a different x-height but are kept in the same fount at the museum (see also the standing type composition, Fig. 4.39).

The two 'C' types that visually appear to be newly cast on a low corpus and that are kept in the tray MPM.V.V.2.6.R64, have an average composition of Pb 87.7 wt% (±0.2), Sb 8.1 wt% (±0.3), Sn 4.0 wt% (±0.2) and Cu 0.2 wt% (±0.05). They are probably much more recent casts.

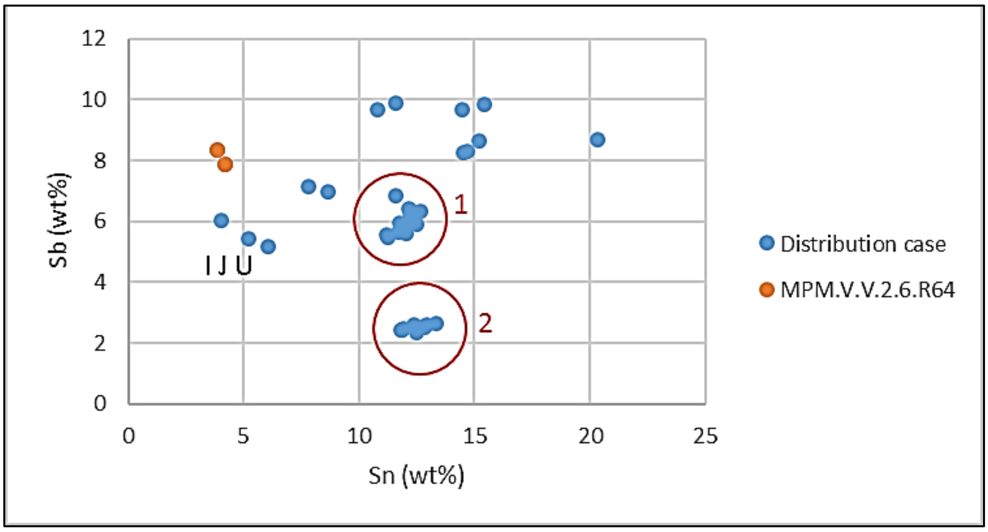

Fig. 4.48: Individual types results from 35 XRF measurements on lead types from ST 3 in the exhibited distribution case and additional two types from the tray V.V.2.6.R64.

Table 4.9: Compositional XRF results of 35 measured types, grouped and indicated by character.

Description	**#**	**Glyphs**	**Composition in wt%**			
			Pb	**Sb**	**Sn**	**Cu**
Group 1	11	A C Q R T Z *Greek:* Ε Υ Φ Ψ Ω	81.9 (±0.7)	6.0 (±0.4)	11.9 (±0.5)	0.2 (±0.04)
Group 2	10	F G K M X Y *Greek:* Δ Θ Ξ Π	84.9 (±0.6)	2.5 (±0.1)	12.5 (±0.5)	0.1 (±0.02)
Group 3	3	I U* J*	89.1 (±0.7)	5.6 (±0.5)	5.1 (±1.0)	0.3 (±0.17)
Group 4	3	H L P	76.3 (±0.5)	8.4 (±0.2)	14.8 (±0.3)	0.5 (±0.19)
Group 5	2	E V	84.1 (±0.4)	7.1 (±0.1)	8.6 (±0.6)	0.6 (±0.11)
Group 6	2	B D	74.9 (±0.8)	9.8 (±0.1)	14.9 (±0.7)	0.4 (±0.09)
Group 7	2	N O	78.1 (±0.3)	9.8 (±0.2)	11.2 (±0.6)	0.9 (±0.39)
Item 8	1	S	70.6	8.7	20.3	0.4

4.3.2.3.5 Initials 'cadeau' 5 lignes d'Augustine petite (ST 79; Lead type Inv. N° MPM.HB.13623, 13652, 13653, 13654, 13655)[7]

The wooden models, listed as ST 79, are boxwood carvings on oak (Fig. 4.49-Fig. 4.51). The total of 21 pattern letters are cut as 1, 2 or 3 characters (about 20 mm x-height) together in the wood, indicating that they have always served as models from which to cast metal type. They seem to be from the same hand as ST 80 (follows) and attributed to Silvius' print shop (Parker & Melis, 1960). The boxwood carvings are attached with glue to the oak base and some excess can be seen at some of the sides (Fig. 4.51). Despite the fact that these characters can never be used for printing purposes, it appears that there are also ink remnants on the wooden surfaces. It cannot therefore be excluded that, at some point in time, someone duplicated the faces by printing them for documentary purposes.

Fig. 4.49: Box with wooden models of ST79.

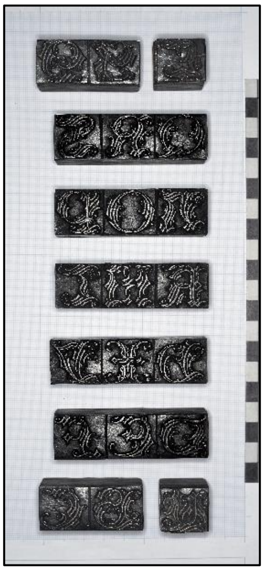

Fig. 4.50: Separate pieces from box ST79.

Fig. 4.51: Upper image: boxwood on an oak base. Lower image: remnants of glue and/or ink.

The lead castings from the above models are nailed onto an oak shank, all characters separately (Fig. 4.52). The complete set exists in the MPM collection as nos. 13597-13655. They are attributed to van den Keere, 1578.

Fig. 4.52: Lead castings of ST 79, wafers of about 3 mm thickness fixed with iron nails to an oak base. Centre photo shows two nails in the centre of the 'D'; the right photo shows a detail of a nail head.

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[7] See also: Max Roose's catalogue N°52 BC

The XRF measurements show the following results: Pb 79.9 wt% (±2.5), Sb 5.8 wt% (±0.1) and Sn 9.3 wt% (±0.3). Results and discussion are presented in 4.3.2.3.8.

4.3.2.3.6 ST 80 (Inv. Nr. V.V.2.6.SK.001)[8]

This set of 24 patterns (on an x-height of c. 12 mm) is also used by Silvius first, and after 1577 by Plantin. As ST 79 they are particular in their arrangement of letter carvings, being cut in bands of 2, 3 or 4 characters at the same time (Fig. 4.53-Fig. 4.54). Therefore, they could never have been used for direct printing , but were made exclusively as models for casting purposes. They are described to be of the same hand as ST 79 (above), 16th century (Parker & Melis, 1960).

Fig. 4.53: Set of wooden characters, cut in pairs of 2, 3 and 4 on the same blocks.

Fig. 4.54: Detail of letters adjacent in the same carving (above) and boxwood letters attached to an oak support (below).

Lead casts are kept in the MPM and the inventory lists: on October 28th 1577 Van den Keere delivered to Plantin '*4 Alphabets de Cadeaulx 96 pieces pesantes lb 8 5/8 Dond je compte de la fonte en Sablon la Justification avec la fonte du Shank et preparation a ce faicte ensemble a 2s la piece – fl 10*' [Arch. 42, p.13]. The total cast type characters, which are present in MPM, consist of 229 pieces. This number does not correspond to the archives as mentioned above.

The faces are cast in sand, while the bodies are separately cast onto the faces. From the total set of 229 characters, all type from A to K were measured at the faces' surface and on the body, giving a total of 190 XRF measurements on 92 pieces. When a bottom was planed, an additional measurement was executed to compare the XRF results between oxidised surfaces and the clean bulk. There were no significant differences to be noted, all results gathered within the standard deviation as indicated in Fig. 4.59.

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[8] See also: Stephen Harvard 'Ornamental Initials', BM.40536, 1974, p.9.

Fig. 4.55: Lead casting from the wooden models of ST 80.

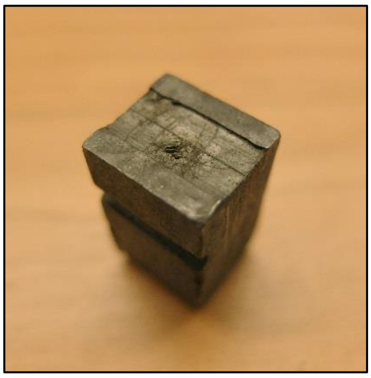

Fig. 4.56: Bottom of the shank with a lowered centre.

Fig. 4.57: Filed bottom of a shank with a shrinkage cavity*.

Fig. 4.58: One of the characters in cast lead, with the face wafer (left) and the cast-on shank.

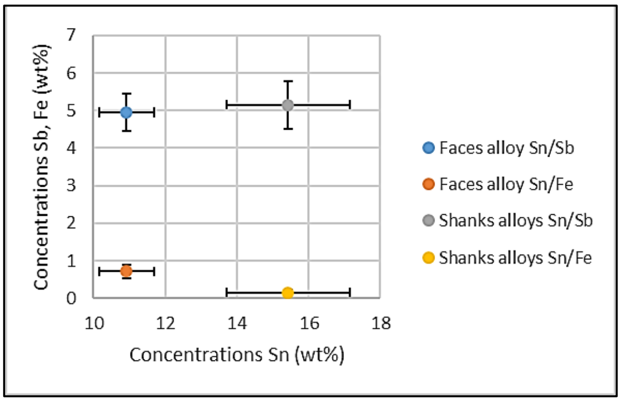

Fig. 4.59: XRF results on the ST 80 lead casts, respectively the faces and shanks for Sn/Sb and for Sn/Fe ratios.

From the results, it has to be concluded that the complete set was cast in one go. The homogeneity of the faces, with an average composition of Pb 82.6 wt% (±0.9), Sn 10.9 wt% (±0.8), Sb 5.0 wt% (±0.5) and Fe 0.7 wt% (±0.2) would imply this. Since the shanks are of a different alloy, Pb 78.7 wt% (±1.5), Sn 15.4 wt% (±1.7), Sb 5.2 wt% (±0.6) and Fe 0.2 wt% (±0.1), also homogeneous for all measured items, it can be concluded that they were cast in one go too, although with on a different moment and with a different batch of lead alloy. Unexpectedly, the shank alloy contains more Sn and has less Fe, which is unnecessarily expensive. Nevertheless, a different batch of lead alloy was apparently used to cast all the bodies onto the faces in one go. It is therefore not likely that this set would be the 96-pieces set as charged for by Van den Keere to Plantin in 1577.

4.3.2.3.7 Initials Roman I with religious scene (Inv. N° MPM.HB.13587, 13590, 13591, 13592, 13595)

Only 12 lead types (nos.13585-13596), mounted as 4 mm thick casts (c. 35 x 35 mm) on wooden supports, survive in the MPM collection. It appears that the lead casts are glued onto the wooden support. They are dated 1850 and are of unknown origin. The measurements have shown the following compositions: Pb 86.8 wt% (±2.1), Sb 8.5 wt% (±0.8) and Sn 0.6 wt% (±0.04).

Fig. 4.60: Five pieces of ‘Initials Roman I’ were selected from the collection for measuring their alloy compositions.

4.3.2.3.8 Discussion on the analytical results on the above lead type groups (4.3.2.3.1 - 4.3.2.3.7)

An overview of the averaged results for each of the measured sets is presented in Table 4.10. As a general observation for the 16th century items as opposed to the 19th century set, tin is prominently present in the alloys over a low antimony content. For the 19th century set, antimony is an important part of the lead alloy whilst tin is very low.

Table 4.10: Averaged XRF results on the historical lead types (4.3.2.3.1 - 4.3.2.3.7).

	Item	Attributed	Year	Pb	Sb	Sn
1	Hebrew type	Le Bé (I)	16th century	54-82	1-11	14-38
2	Initials Cadeau	Unknown	1575	80	0	18
3	ST 1	Van den Keere	1575	71-94	2-7	4-12
4	ST 3	Sabon – Vd Keere	1565 - 1571	71-89	3-10	5-20
5	ST 79	Van den Keere	1578	80	6	9
6	ST 80 Faces	Van den Keere	1577	83	5	11
7	ST 80 Shanks			79	5	15
8	Initials Roman I	Unknown	1850	87	9	1

More specifically, three groups can be distinguished: 1) the Initials ‘Cadeau’ (N°2 in Table 4.10) are with the highest tin content and almost no antimony; 2) the Hebrew types (N°1) and the types of Van den Keere (N°3-7) with high tin concentrations but also with an average of 6 wt% antimony; and finally 3) the 19th century Initials Roman I (N°8), which are very low on tin (1 wt%) but with a higher concentration of antimony at 8-9 wt%.

In Group 1, with the Initials Cadeau types, the pins that were used to fix the faces to the wooden shank are not shown in Table 4.10 as they are not representative as a type alloy. They were most probably used to 'solder' the back of the faces into the wooden support, as the metal was poured into the holes from the back (see 0). Their composition, Pb-Sn 52-48 wt% (Fig. 4.61), has a melting point of about 220°C (see Pb-Sn phase diagram in Chapter 2). The faces (Pb-Sn c. 80-18 wt%, Fig. 4.62) have a melting point of about 280°C, which can easily resist the lower temperature of the alloy poured in for the pins. Moreover, the faces contain almost no Sb (Fig. 4.63, Fig. 4.64), which also separates them from the other types in this list.

Group 2 holds the Hebrew types from Le Bé, but these are perhaps cast by Van den Keere. Sets ST 1 and ST 3 have results that match very closely (Fig. 4.36, Fig. 4.37, Fig. 4.48), in composition but also in the wide variation between the individual types that were cast. Sets ST 79 and ST 80 also match very closely and show much less variation in composition (Fig. 4.62-Fig. 4.64). It is known that Van den Keere billed Plantin in 1571 (Parker & Melis, 1960) for casting lead on ST 3, most probably from matrices set MA 78. Sets ST 79 and ST 80 would date from 1577-1578 with a higher consistency in alloy composition (Table 4.10). The Pb/Sn and Sb/Cu ratios of ST 80 show that the faces and the shanks were cast separately, but each part most probably in one go (Fig. 4.62-Fig. 4.64).

Group 3, which holds only the 19th century Initials Roman I, is deviant from all previous and most probably 16th century results with its very low Sn and relatively high Sb concentration (Fig. 4.62, Fig. 4.63). The large variation in Cu concentration is perhaps due to a copper-based ink that was left on the surface.

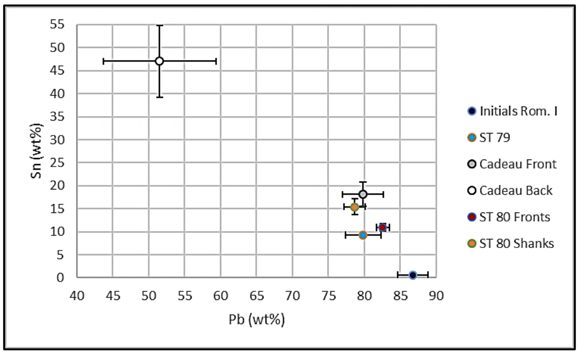

Fig. 4.61: XRF results Pb/Sn ratios of all types from selection 3.

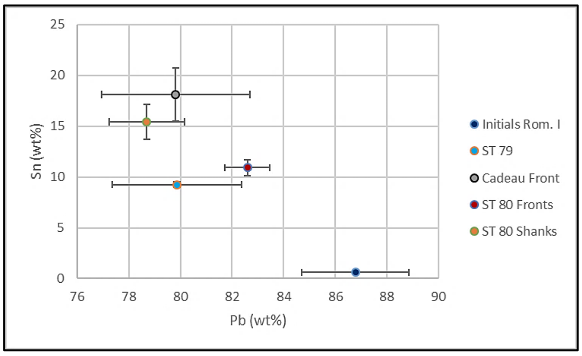

Fig. 4.62: Detail of the XRF results in Fig. 4.61 for the 77-89 wt% Pb range.

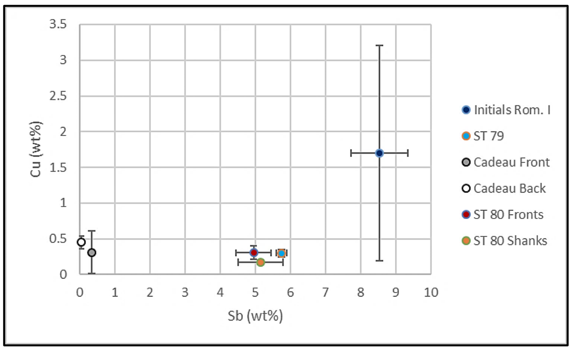

Fig. 4.63: XRF results for the Sb/Cu ratios.

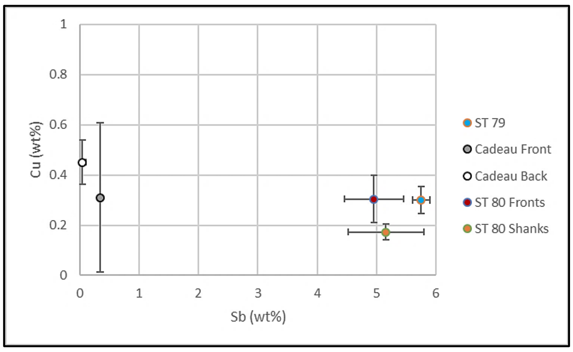

Fig. 4.64: Detail of Fig. 4.63, excluding the 19th century Initials Roman I.

4.3.2.3.9 Brass letters (Inv. N° HB.13658, 13659, 13669, 13660, 13673)

As a complementary set to the lead alloyed printing blocs and type, there were also brass models in use for direct printing, as opposed to the brass matrices (see Chapter 2). They are single capital characters in square format with flower-like ornaments (c. 13 x 13 mm), mounted on a wooden shank and estimated to date from around 1600 (Fig. 4.65-Fig. 4.68).

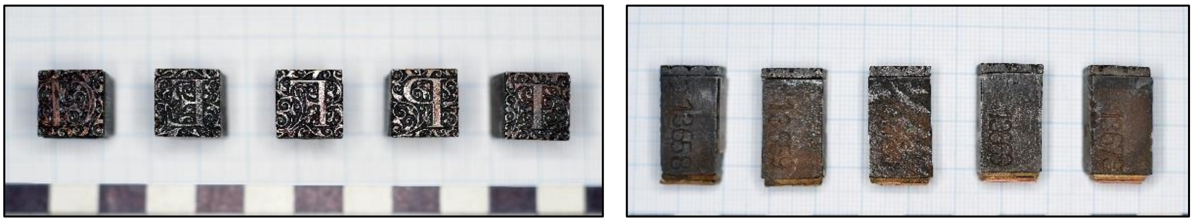

Fig. 4.65: Faces and sides of the five measured items from the brass types set.

Fig. 4.66: Detail of one of the faces, showing remnants of ink and probably a lacquer coating.

Fig. 4.67: The face of 'X' was detached from the body. A solder mark is visible.

Fig. 4.68: Detail of the side, with burrs from engraving directly in the brass sheet.

The composition[9] of the brass has an average of 64 wt% Cu, 31 wt% Zn, 2 wt% Pb and traces of Fe and Sn. The burrs on the sides (Fig. 4.68) indicate that the pieces were cut to measure and subsequently engraved directly into the brass. In this case, no sandcasting or other duplicating technique was used. The solder patch at the back (Fig. 4.67) is probably left from mounting the piece onto a larger substrate for easier handling during engraving. This could have been a larger sheet to be used on a leather cushion or perhaps mounted in an engraver's ball socket. Low melting lead-tin alloys can easily be used for temporary fixing onto a larger substrate, although pitch* or shellac* were also frequently used for this purpose.

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[9] The composition of the brass pieces was analysed using the Olympus-InnovX Delta XRF instrument, used and calibrated as described in chapters 3 and 5.

4.3.2.4 Discussion

The dating of type is often an important question, but it cannot be derived from the alloy compositions as such. Only extensive measurements on preferably dated samples (e.g. archaeological finds) could provide insight. Dating historical type can only be achieved firstly when type casters would have used more or less 'standardised' alloys, secondly they had to achieve a fair homogeneity in their cast sets and thirdly when a clear evolution in the alloy compositions through time is proven from the results.

Taking the archaeological finds into account, what the three locations (Lyon, Wittenberg and Kralice) dating from the 15th to the early 17th centuries seem to have in common is that the type alloys are mainly lead-based with additions of tin and antimony. The Wittenberg finds also present bismuth as an alloying element.

Specifically for the types from Lyon (15th to 16th century) the results show that there is lead, tin, antimony and iron present while in some cases also silver has been found. The Kralice types (16th century) have a mean average composition of 79 wt% lead, 14 wt% tin, 6 wt% antimony and 1 wt% iron. The types from Wittenberg (16th to 17th century) are the most detailed and show three groups of alloy compositions: lead with balanced parts of tin and antimony at 8-10 wt%, 5-10 wt% and 10-5 wt% tin-antimony respectively. The bismuth concentration seems to be related to the tin content.

Results from the measurements on types in the Plantin-Moretus Museum, dated most probably 16th century, are in accordance with the above findings, although a broad variation in composition is present. As introduced in 4.3.2.3.8, three groups of lead alloys are revealed respectively as being without Sb (Initials Cadeau), with relatively high Sn and low Sb (mostly connected with founts by Van den Keere), and finally the 19th century types with high Sb and low Sn.

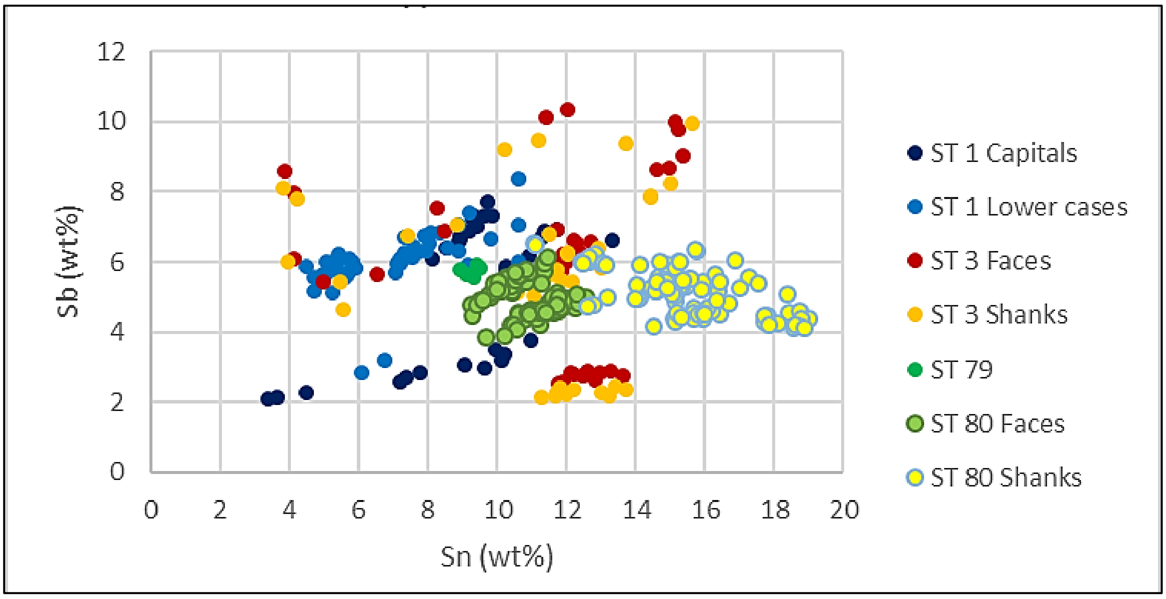

Fig. 4.69: Sb and Sn concentrations obtained from all XRF measurements on the individual lead types from sets ST 1, ST 3, ST 79 and ST 80.

In relation to group 2 and the individual measurement results, an overview of all results is given in Fig. 4.69. These founts, which are attributed to Van den Keere, cannot easily be interpreted. Some observations can be made, however, such as the wide variation in lead compositions of ST 1 and ST 3. The lower case of ST 1 is nonetheless somewhat more concentrated between 5-8 wt% Sn and at 6 wt% Sb. From ST 79 only five measurements were taken, but they are very closely concentrated at 9 wt% Sn and 6 wt% Sb. The fount of ST 80 is quite homogeneous, certainly for the faces, which have an average composition of about 11 wt% Sn and 5 wt% Sb. The shanks are cast onto the back of the faces with another alloy, containing more Sn (average 15-16 wt%), which is unnecessarily high and costly.

As a minor metal, copper seems to be most prominent in the Antwerp types, while no bismuth was found in the German types. From a metallurgic point of view, copper in the types is not uncommon, since pewterers used this metal in the production of tinware to make a stronger alloy.[10] Therefore, it was already known that this element would make the type harder and better able to withstand the printing process. When tin with added copper was recycled, a relationship between the copper and tin content could be expected. Another source for the copper content can be found in the use of old solder from stained-glass windows. This tin-lead solder would have contained some copper from the soldering rod used to make the leaded window panels.

4.4 Conclusions

It was possible to compose a set of reference alloys to represent most of the historical type metal alloys. Evaluation with ICP-OES showed that the accuracy of the alloys lies within small margins, making them suitable as a reference set. This set enabled the experiments that show microstructures and the hardness values.

The metallographic images revealed a wide range of varied microstructures in the Pb-Sb-Sn alloys, as could be expected from literature. Binary Pb-Sb and ternary Pb-Sb-Sn alloys were studied for their phases in composition and distribution throughout the bulk. As opposed to the theoretical phase diagrams, at room temperature a higher dissolution of Sb in Pb-rich phases is noticed (4 wt%). This is due to the rapid cooling of the castings, as can also be expected with cast types. The Sb-rich phases in the binary Pb-Sb alloys show a average ratio of 92:8 wt% Sb:Sn for the alloys 84-16 and 80-20 Pb-Sb. The SbSn phases in the ternary Pb-Sb-Sn alloys show a ratio of 31:41 wt% Sb:Sn in the alloy with 8-12 wt% Sb-Sn and 83:13 wt% Sb:Sn in alloy 16-4 wt% Sb-Sn. The SbSn phases in all other ternary alloys show an average ratio of about 50:35 wt% Sb:Sn. The different Sb-Sn ratios in these phases have an influence on their potential compared to the surrounding Pb-rich matrix. Electrolytic measurements on microscale would be beneficial to measure these differences but were beyond the scope and the instrumental possibilities in this study.

Vickers hardness measurements were performed to objectivise the influences of the Sb and Sn additions to the lead. In line with the literature, increasing hardness values were found with increasing levels of Sb and Sn. However, the differences in hardness are relatively small when Sb and Sn are added to the lead. There is a general hardness value increase from 4 to 15 HV when at least 5 wt% Sb is added

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[10] The Worshipful Company of Pewterers had different grades of pewter in the 16th century, when ‘fine metal’ used for tableware contained about 1% copper.

to the lead. When adding Sn too, there is a further increase of hardness to about 20 HV (±5). As a consequence, small differences in Sb or Sn concentrations in the range of respectively 5-16 wt% Sb and 4-12 wt% Sn have no significant effect on the hardness values and therefore also not much effect on the physical resistance of the cast type in the course of printing. Considering that printers searched for the hardest alloy at the lowest cost, it is confirmed that an alloy with 12 wt% Sb and 4 wt% Sn would have been the best choice, with a hardness of 22 HV. This alloy is equal to the ternary eutectic point.

Portable XRF analysis was examined for its accuracy in measuring and in calculating quantitative data from the spectrum, using the built-in software programs. Acquiring a spectrum for the elements in type alloys is not an issue for any of the instruments since the element peaks do not overlap with each other. There are, however, some facts to consider when using quantitative data. First, for all software programs there is a systematic under-estimation of the numeric values for the antimony and the tin concentrations. Moreover, the quantification of tin varies with the presence of higher antimony concentrations, probably due to secondary fluorescence effects. This makes a mathematical correction on the numeric results difficult. In this respect, the Olympus-InnovX Delta showed the least deflection.

The experiments have shown that portable XRF has great potential from a conservation perspective, primarily for its ease of use, its speed and its ability to define alloy compositions within small margins of error. For other research purposes, different analytical techniques should be used for more detailed results on the alloy compositions, especially concerning trace elements.

SEM-EDX was also applied to the reference alloys for the bulk concentrations and for the individual phase compositions. It was found that quantitative data for the bulk measurements was constantly over-estimated with the standard INCA software settings for measuring the concentrations of Sb and Sn in the bulk alloys. Moreover, in some cases the results for the deflections of particular element depended on the concentrations of other elements in the matrix. Despite the fact that the instrument was calibrated using external metallic elements of Pb, Sb and Sn, numeric results were significantly different from the actual alloy compositions. It was probably the presence of very different phases within the measured area that caused the errors. The measurements on the individual phases with spectra from points or small areas seem to give more accurate results. As a result, quantification of Pb-Sb-Sn alloys should be checked with a set of standardised alloys. If needed, the INCA software settings have to be adapted accordingly.

The results of the XRF measurements on lead type in the Plantin-Moretus Museum collection indicate that the alloy composition varies from tin-rich and low-antimony in the 16th century to low concentrations of tin and high contents of antimony in the 18th and 19th centuries. This is in accordance with historical sources on type metal compositions. The measured compositions also show that the alloys that were chosen for the production of the reference set, correspond largely with the ranges of tin and antimony concentrations in the lead type alloys.

In addition to the extensive historical research performed on the collection of the Plantin-Moretus Museum, material research offers additional information. The results enable former findings to be confirmed, or questioned in some cases. Further and more extensive measurements on the collection may provide insights into the homogeneity of the castings and possibly reveal more recent additions or replacements.

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5 On the composition of copper matrices

Publication related to this chapter:

Storme P., Fransen E., De Wael K. and Caen J.: ‘*X-Ray Fluorescence as an analytical tool for studying the copper matrices in the Museum Plantin-Moretus collection*’, in Golden Compasses Jg. 95-1 (2017), p. 7-33.

Content

5.1 Introduction

The collection of the Museum Plantin-Moretus includes, amongst many other items, sets of copper matrices, which are the ‘dies’ for casting types. They are of great interest for typography research and have been studied intensively in past decades, mainly through visual comparison and sustained research in the Plantin archives and books, which were printed with type cast from the matrices. Until now, there has never been an attempt to apply analytical measuring techniques. The main reason for this is the vast number of strikes and matrices (about 20,500 pieces) and the fact that they cannot leave the museum and cannot be damaged for destructive analysis. In addition, the majority of matrices are made of copper and were never questioned towards possible variations in material composition to differentiate them from each other. X-Ray Fluorescence (XRF) is used to provide analytical results on the copper compositions.

Research on matrices can contribute to knowledge about the origin and history of typecasting and typefaces. It can help to define precise sources from which matrices for the types reached a printing office, in this case Plantin. Since the earliest records on handprinting, the use of steel punches to strike copper matrices is predominant according to the abundance of studies. At first sight, therefore, it doesn’t seem worth trying to analyse these pieces. However, copper was never completely free of trace metals, at least not until the 19th century when advanced chemical techniques upgraded the copper purity. The reason for the presence of other metals in the copper lies in the method of unearthing the ore, the smelting processes and the refining techniques used at the time. Therefore, it could be expected that each batch of ‘pure’ copper that was sold on the market contained some trace metals. Since it is known that coppersmiths provided copper to the punchcutters/matrix-maker in the form of rods, which they had cut and hammered from large sheets or blocks (Fournier, 1764), possible tendencies in the presence of trace metals could be found.

The goal of this study, using XRF as an analytical technique, is to determine the alloy composition(s) used in each set of matrices to indicate possible alloy composition deviations of certain matrices within a set. Furthermore, by performing an extensive series of measurements on the matrices’ collection, it could perhaps lead to the detection of possible tendencies in the copper composition used by a particular punchcutter to whom a set of matrices is attributed. Similarly, possible tendencies of copper used in different locations and through the centuries could emerge. Finally, it might be possible to identify the punchcutter-matrix maker of non-attributed matrices sets, although this goal may be far beyond our reach. At the very least this work will complement the extensive studies historians and typographers have conducted over the last century.

Various difficulties emerged in this study, for instance the punchcutter’s active period in time. This often covered several decades, which means that it is nearly impossible for one person to have used only one kind of copper. A second difficulty is that, at the time, they were unable to quantify the quality of their copper for making the strikes. Although they preferred to work with the purest and softest copper, so as not to damage their costly punches, they had to rely on the coppersmith, from whom they purchased copper rods, and on their own skills to evaluate the copper whilst striking the punches. A third difficulty in attributing copper qualities to a person, city or time period is the lively trade in metals during the 16th century. Copper could find its origin in almost any part of Europe and could have been purified in different ways, leading to a wide range of compositions. Although ‘pure’ copper was used, the refining techniques were relatively primitive and lead to a purity level of about 99%. The remnant consisted of traces of other metals, such as lead, antimony, silver, and iron. Therefore, the measuring campaign focusses firstly on the ability to distinguish copper qualities from each other, and secondly on possible trends between makers, cities or periods in time.

Another obstacle is found with producing the strikes with the steel punches, made by a certain punchcutter. Mid-16th century the striking is mostly done by the punchcutter himself, but in the event that he had sold his punches, anyone who owned the punches from then on could have produced a set of strikes – or even multiple sets for sale across Europe. Although the matrices that have survived in the MPM collection have been studied extensively (see Chapter 2) to determine the cutters of the types, attributing the copper composition to a person or a region is not always straightforward, especially if there are no archival documents to support a trade or an acquisition.

In any case, the copper strikes and matrices in the MPM collection are amongst the best documented pieces of 'pure' copper that exist from the 16th century onwards. Together with so-called 'insculpatie-platen' (metal sheets on which goldsmiths had to register their hallmarks each year), material-based information can be gathered from them. Regarding the production of strikes, the matrices in the MPM collection are acquired in a wide time window and the origin of specific matrices sets has until now been based exclusively on archival documents. From these written sources, a relatively small number of punchcutters/strike-makers are known or are assumed to have produced strikes that are still in the MPM collection, whether as strikes or as justified matrices (Lane, 2004).

5.2 Experimental

XRF is used as an analytical technique to measure the composition of the mainly copper matrices. This technique was chosen for the speed with which it measures and delivers data, for its non-invasive character and for its portability, which enabled the matrices to be measured in the Plantin-Moretus Museum (MPM) itself. These requirements are necessary because the collection comprises many thousands of matrices, which, to prevent loss or theft, may not be sampled nor leave the museum.

5.2.1 Reference materials

The XRF instrument provides compositional data, retrieved from the spectrum that is measured on each of the matrices. The quantification of the elements has been verified with measurements on IMMACO standardised copper alloys. These alloys were designed to act as references for historical copper alloys (Beldjoudi, 2001). The five IMMACO copper alloy compositions are listed in Table 5.1.

Table 5.1: Elemental compositions of the five respective IMMACO standardised copper alloys.

IMMACO	Cu	Pb	Sb	Zn	Sn	Fe	Ni	Mn	As	S
1.7.52	76.50	9.00	0.50	6.00	7.00	0.20	0.10	0.20	0.20	0.30
2.7.54	93.40	0.20	0.50	0.00	0.20	0.20	0.00	0.20	5.00	0.30
3.2.24	90.20	0.20	0.70	0.10	7.00	0.30	0.50	0.30	0.20	0.50
4.1.41	78.80	10.00	0.30	0.10	10.00	0.10	0.30	0.10	0.30	0.00
5.9.2	81.10	0.40	0.00	15.00	2.00	0.50	0.20	0.40	0.10	0.30

5.2.2 Graphic presentations

As a guideline and aid for the reader, the graphic presentations in this chapter are explained here.

In the first part, ‘Phase 1’, most graphs represent all individual XRF measurement results as dots. Since the most prominent metals in the matrices (besides the copper) seem to be Pb and Sb, graphs show these elements pairwise, as shown in Fig. 5.1. In this particular graph, the matrices for W and AE deviate strongly because they are made of brass (copper with zinc) instead of ‘pure’ copper. For visual consistency and easy comparison, all graphs except for a few, have a scale from 0 to 1.2 wt% Pb on the x-axis and from 0 to 1 wt% Sb on the y-axis.

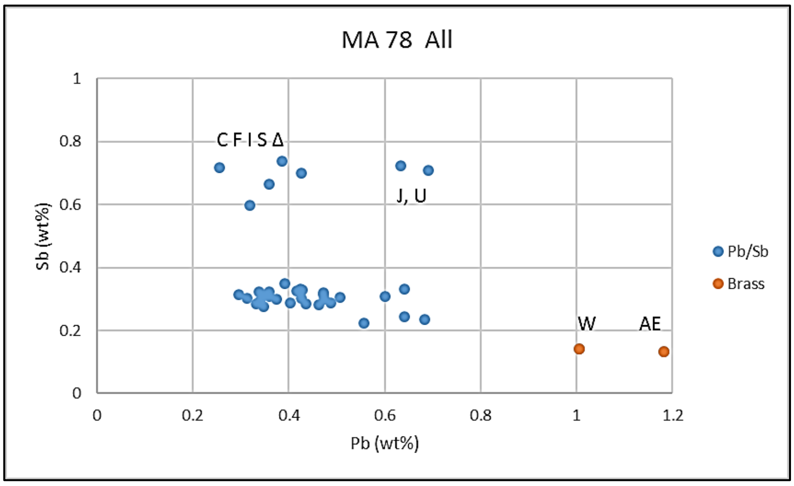

Fig. 5.1: Every dot represents an individual matrix XRF result, for the metals Pb (x-axis) and Sb (y-axis) in the copper, indicated as wt%.

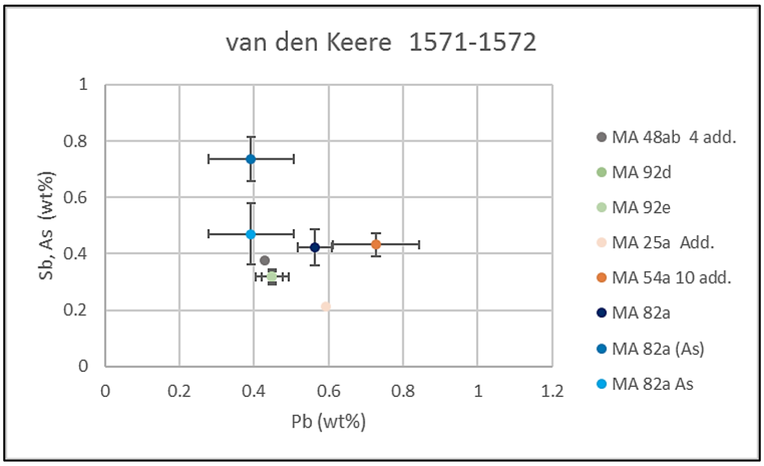

Fig. 5.2: Averaged XRF results as dots for a number of sets of matrices. Pb is plotted on the x-axis while Sb and As are shown on the y-axis and indicated differently in the legend.
For each group, the standard deviations for each element are indicated by bars.

If XRF results of the compositions of matrices are presented as groups, averaged results including standard deviation bars on the x- and y-axis are used as in Fig. 5.2. In some cases, in addition to Pb and Sb, As is also present. If so, the As content is also shown on the y-axis. This graph shows MA 82a three times. The first 'MA 82a' indicates the group of matrices without As. 'Ma 82a (As)' indicates the group that contains As but show the results Pb/Sb. 'Ma 82a As' gives the XRF results for Pb/As.

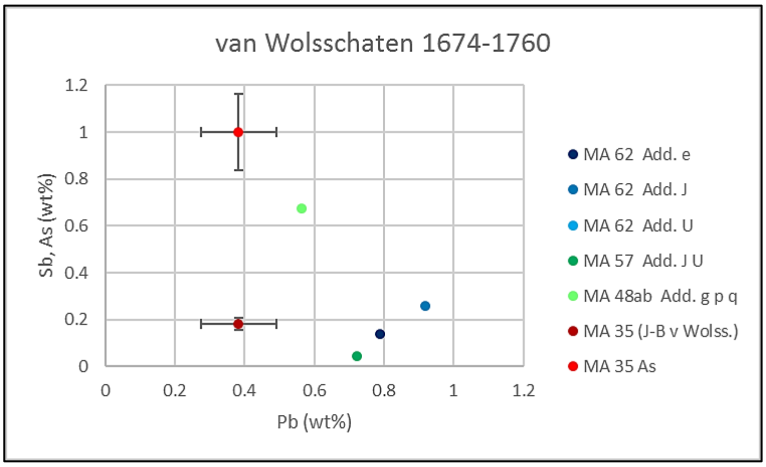

Fig. 5.3: This graph represents the XRF results for four individual matrices and two groups with their standard deviation bars. In this case MA 35 is presented for the Pb/Sb concentrations (dark red dot) and for the Pb/As contents (bright red dot), denoted as 'MA 35 As'.

A few sets of matrices consist partially or completely of brass matrices. In these cases, a separate graph is presented with Zn and Sn respectively on the x- and y-axis (Fig. 5.4).

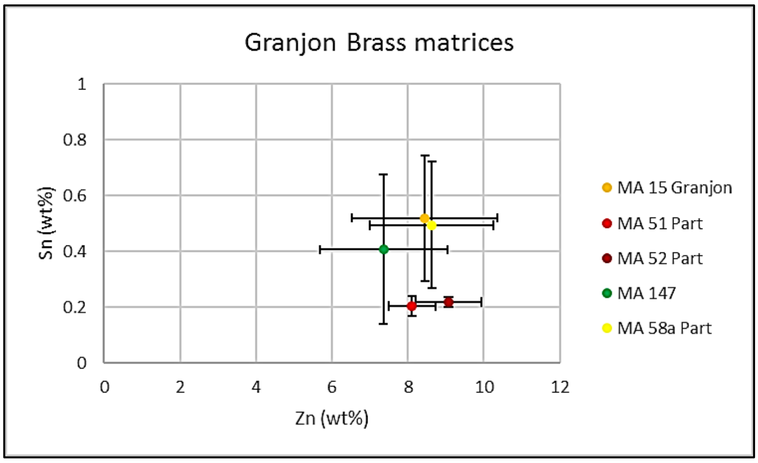

Fig. 5.4: The XRF -results for brass matrices are represented with an additional graph, showing the Zn and Sn contents, complementary to a previous graph with the Pb and Sb concentrations.

5.3 Selection of matrices from the MPM collection

A two-step phase approach was chosen, with the first phase evaluating the XRF measurements and the viability of the results. This first step is referred to henceforth as 'Phase 1' and has already been published (Storme, Fransen, De Wael, & Caen, 2017). Based on these results, a second phase of measurements on a larger number of matrices was carried out with a select choice of matrices; detailed information on these was available in the Plantinian archives. Additionally, another group of matrices was selected on their aberrant visual appearance.

5.3.1 Phase 1

For the purposes of evaluating the XRF technique, a choice amongst matrices sets in the MPM collection was made. Five sets of strikes, attributed to Robert Granjon (°1513-†1590), were selected. These are the strikes MA 120, 134, 156, 184 and 191, for 'Jolie Cursive' (Fig. 5.5). Besides the fact that they have a very similar visual appearance and they were probably never used for casting type, we know from the Plantin archives that the strikes were purchased as a lot of 11 identical sets from Granjon in 1574, together with the punches (ST 30). The six other sets are no longer known to exist.

MA 120 MA 134 MA 156 MA 184 MA 191

Fig. 5.5: The five selected strike sets 'MA 120 etc.' from the Plantin collection. MA 156 is missing the capitals.

With reference to the strikes in sets MA 120, 134, 156, 184 and 191 (further denoted as 'MA 120 etc.'), the Inventory (Parker & Melis, 1960) mentions: "Caps, lc, lig, acc, nos, punct, 111 strikes. MA 156 consists of lc, acc, nos, punct, 77 strikes".[1] Furthermore, it is written in the archives that in October 1574 Plantin paid Granjon for 11 strikes with the punches [Ar. 98, pp. 257, 265, 277]. One of these he exchanged with Van den Keere for his Jolie Romaine in May of 1575 [42 p 7v°; 153 pp 160, 165]. On Van den Keere's death in 1580 he had a strike of '*Jolye Cursyve van granjon*' [Inv vdK 1580], which Plantin bought back from his widow since it does not occur in De Vechter's post-1581 Inventory. None of the others appear in the 1581 Inventory and so were probably in Frankfurt. In 1588 in Frankfurt, there are '*7. Sept frappes de corsive nonpareille de Grandion contenant chacune frape 111 matrices'* [Inv Frank 1588]. In 1589-90 there were 6 in Frankfurt, 1 in Antwerp and 4 in Leiden, all of 111 strikes, in sum the original 11 sets [Invs Ant 1589, Frank 1590, Leid 1590]. The [1590] Frankfurt and 1590 Frankfurt-Leiden Inventories show that five of the Frankfurt six went to Moretus, the other one to Raphelengius, making five in Leiden and six in Antwerp; these six were still there c. 1612. The 1652 Inventory seems to list only one strike, but the 18th century inventories list ten.

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[1] Caps: Capital letters; lc: lower case; lig: ligatures; acc: accents; nos: numbers; punct: punctuation marks.

The surviving sets of strikes, MA 120 etc., all have sloping capitals which appear to belong originally with the sets. At any rate they were cut before March 1579 when Van den Keere justified matrices for them for MA 71 (Parker, Melis, & Vervliet, 1960).

The Van den Keere Inventory of 1580 (Ar.153, p.295-303), List C (Ar.153, p.299-297) (Parker, Melis, & Vervliet, 1960) mentions under '*Dit syn rau afslaghen'* (These are unjustified strikes) MA 120 etc. '*Jolye Cursyue'*. A note is also added: '*Noch so esser seer veel copere dwelck al bereyt is an afslaen van alle soorten'* (And there is also a lot of copper which has already been prepared to make strikes of all sorts). When Plantin and De Vechter (foreman in Van den Keere's foundry) acquired all the material from Van den Keere's workshop, we can assume that they would produce strikes themselves or order them from a subcontractor; these copper rods could have been used until the stock was exhausted.

MA 71 is a set which has been justified, while the other sets (above) are strikes which were ordered by Plantin for resale to other printers. All the above matrices were struck with the punches ST 30 from Granjon's hand (except for the numbers). The lower case would have been cut in 1573 or before, whilst the capitals probably date from 1573 or 1574 and were used by Plantin from 1575 on. It is thought that the first set was only equipped with Roman capitals, making this set a composition of different series of matrices. Between August 26th and November 29th 1573 Plantin paid 71 s 5d for '*Les matrices de granjon cursive nonpareille'* and 4s 8d '*A s granjon pr reste des matrices susdites' [116 p 285]*. Between October 14th and 17th Van den Keere charged Plantin '*Pour la preparation du moulle de la plus petite nonpareille / et celuy de ma nomp flam pour faire les 2 epreuves de la petite Cursive de Granjon' [153 p 150].* On September 24th 1574 he sent '*la première partie de la Cursive Jolie en 2 mandes' [153 p 153, 42 p 1]*. On November 25th he sent '*La fonte des pet. Cap. De la Coronelle sur la Jolye / qui est l'accomplissement de la fonte entiere de la Cursive Jolye' [153 p 155, 42 p 2].* The Bible small capitals seem to have been found more suitable later. On March 10th 1579 he sent a font of '*Capitales couchées de la Jolye Cursive'* and charged for justifying the 23 matrices *[153 p 197, 42 p 18].* The 1581 Inventory lists a Jolie 'C*ursive de Robert Granion / justifiée and the 1590 Leiden '164 Jolie Italique justée*'. The c 1612 Octavo Inventory lists '*164 Jolie Cursive'* and the 1652 '*140 Jolie Cursive'*. Possibly in the latter, the matrices for the Coronelle small caps have been removed, perhaps to MA 76 (N° 82) (Parker & Melis, 1960).

Fig. 5.6: Justified matrices MA 71

Matrices set MA 71, consisting of 'Upright caps, sloping caps, lc, lig, acc, nos, punct, 137 matrices (137 minus de caps. curs. 25 + AE = 111, matching the strikes), the numbers not being from ST 30. The upright capitals are the small capitals to Garamont's Bible Romaine [N° 77].' This set would already have been acquired in 1573, although it does not appear together with the 11 sets of strikes in the 1580 inventory. It does appear in the 1581 inventory as 'Cursiue de Robert Gronjon justifiée'. Perhaps it was not complete at that point and was therefore not listed. It was possibly without any capitals since he added a fount of small capitals from the 'Coronelle Romaine' to serve as the capitals (Ar. 153, p.155; Ar.42, f.2). This idea is supported by the texts which are attributed to this type, consisting only of the Jolie Cursive with upright capitals (Parker & Melis, 1960).

5.3.2 Phase 2

From the 200 matrices sets at the MPM, besides the matrices in Phase 1, 105 others were selected. To clarify: set MA 1, for instance, is compiled of MA 1a and MA 1b. This subdivision for sets of matrices gives 201 sets, subsets and particular attributed matrices in total, from 105 matrices boxes. The first group concerns 65 identified and described sets or partial sets of matrices. This selection was done on the basis of their description (Parker & Melis, 1960) and the presence of direct archival notes. A second group was selected on possible attribution to a certain punchcutter/matrix-maker and a third group of selected matrices was chosen on visual aspects, in particular a more yellow colour that would point to brass rather than copper matrices. The final and fourth group comprises the other sets. A full overview of the selected matrices sets is listed in the Appendix, under 'selection'. In brief, it concerns the following matrices:

Group 1, on archival references:

Punchcutter/Matrix-maker	Year	Matrices sets or matrix additions (denoted *)
Hendrik van den Keere	1569-1580	MA 1ab 4 21* 25a* 48ab* 54a* 54b* 58a* 62 67* 68 70 78 82a 91ab 92de 93 96 102 142* 160* 161
Guillaume Le Bé I	1551-1573	MA 6 40 47a 72 97
Robert Granjon	1545-1574	MA 11 15 24* 54a 118 119 120 121 122 128 134 156 182 183 184 191
François Guyot	1562-1567	MA 34 56a* 57
Johan Michael Smit	1732-1736	MA 15* 25c 26b 49a* 56a* 58a*
Thomas De Vechter	1582	MA 96*
Peeter Van Wolsschaten	1674-1690	MA 48ab* 57* 62*
Jean-Baptiste Van Wolsschaten	1760	MA 35
Jacques François Rosart	1758	MA 45 46 151

Group 2, on circumstantial attributions, uncertain dates:

Punchcutter/Matrix-maker	Year	Matrices sets or matrix additions (denoted *)
Hendrik van den Keere	1561-1575	MA 3ab 20abcd 30 76 144 145 148 188dehimno
Claude Garamond	1558-1563	MA 48ab 59 60 188l
Guillaume Le Bé I	1561-1568	MA 2 3a 18 20abd 25a 66a
Guillaume Le Bé II	1581-1652	MA 83a
Robert Granjon	1560-1579	MA 7 8 23 25b 26a 27a 36b 47b 49ab 51 52 53b 54b 58a 63 71 101c 110 126 147 172e 188fg
François Guyot	1555-1567	MA 27a 31 36ab 53b 56a 58a 69 101c 153
Pierre Haultin	1561-1567	MA 32 66a 67 111 140 141 142 143 158 160

(via) Silvius	1567	MA 21
Tavernier	1561	MA 163
Johan Michael Smit	1732-1736	MA 22b 27bc
Franciscus Raphelengius	1590-1652	MA 30 73ab 126
Bomberghens	1565	MA 24 135bc 167a
Hand A	16th C	MA 164c

Group 3, on yellowish appearance:

Punchcutter/Matrix-maker	**Year**	**Matrices sets or matrix additions (denoted *)**
Granjon	1561	MA 15
Granjon ?	1560-1561	MA 51 52 147 172e
Granjon ? Guyot ?	1561-1562	MA 58a
Granjon ? Guyot ? Smit ?	1563-18th C	MA 27a
(via) Silvius ?	1567	MA 21
Unknown	18th C	MA 10

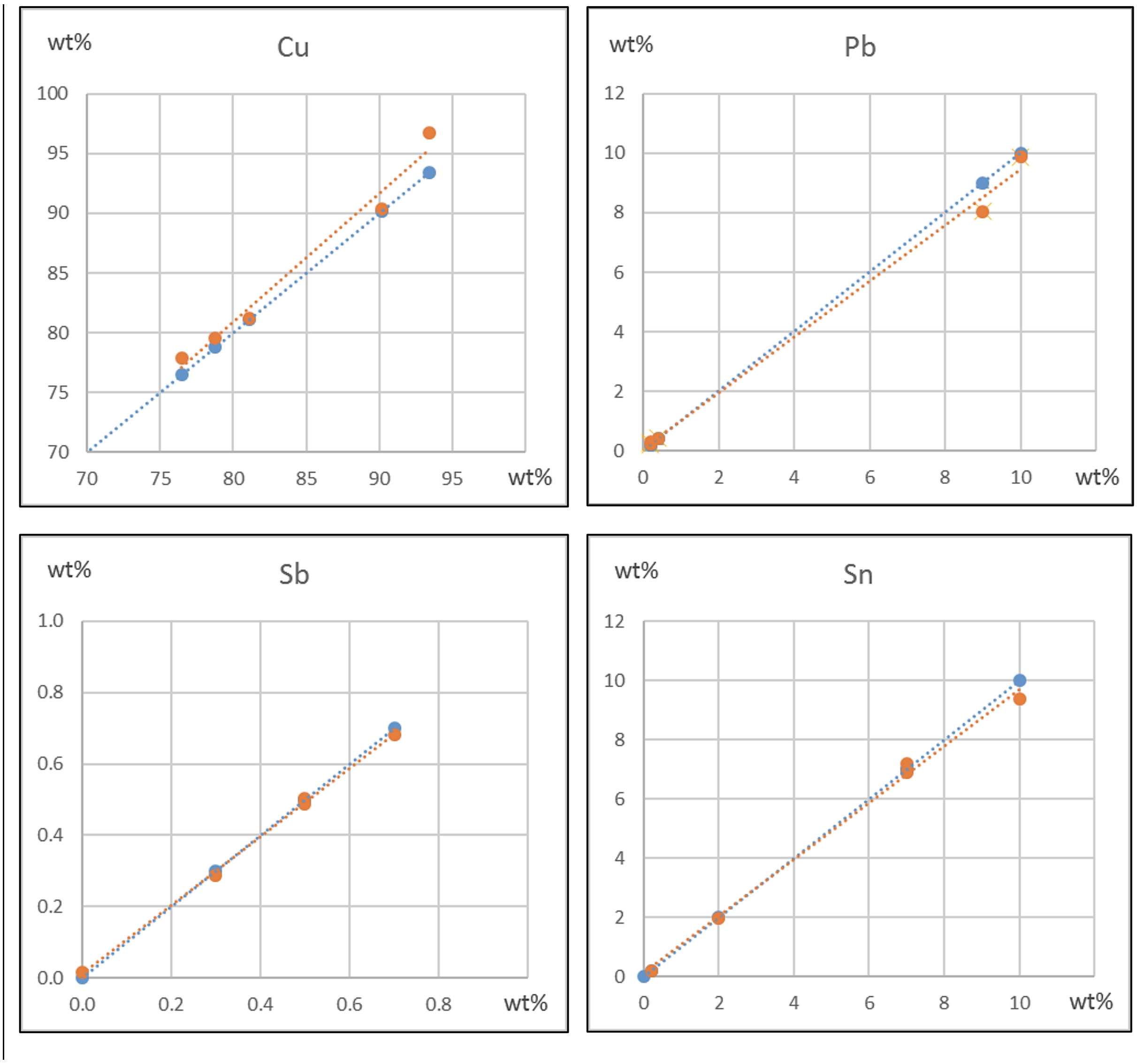
Group 4, others:

Punchcutter/Matrix-maker	**Year**	**Matrices sets or matrix additions (denoted *)**
Unknown	15th-16th C	MA 5a 5b 131a 167b
Unknown	16th C	MA 27d 53a 66b 83b 83c 131b 135a 164a 171 172abcdfg 174 188jkps 146 79b 22a
Unknown	16th / 18th C	MA 77
Unknown	17th-18th C	MA 58b
Unknown	18th C	MA 47c
Unknown	19th-20th C	MA 188abc
Unknown	?	MA 28 56b 79a 117 188r

5.4 Results

5.4.1 Reference materials

The composition of the five IMMACO copper alloys is listed in Table 5.1. Since the measurements are on the limits of detection by the XRF instrument, and the numeric results given in weight percent (wt%) for the elements, there may be some slight deviations. It should also be remembered that XRF is a semi-quantitative technique where the values in wt% are derived through software calculations from the spectrum. The XRF results are shown in Fig. 5.7, listing the most prominent metals that are present in the matrices. The analysing technique permits the detection of tendencies, groups and deviations in alloy compositions. The limit of detection of trace metals in the copper lies around 0.1 wt%. Smaller concentrations are not usually measured by the instrument nor are they taken into account in the results. In addition, the selected mode of the instrument (Alloy mode) discards lighter elements such as sulphur (S). These values are also not taken into account, for two reasons. Firstly, the selected mode quantifies the metallic elements in wt% to a high optimum; secondly, oxidation layers containing S may be present on the measured matrices, which would lead to uncertain results.



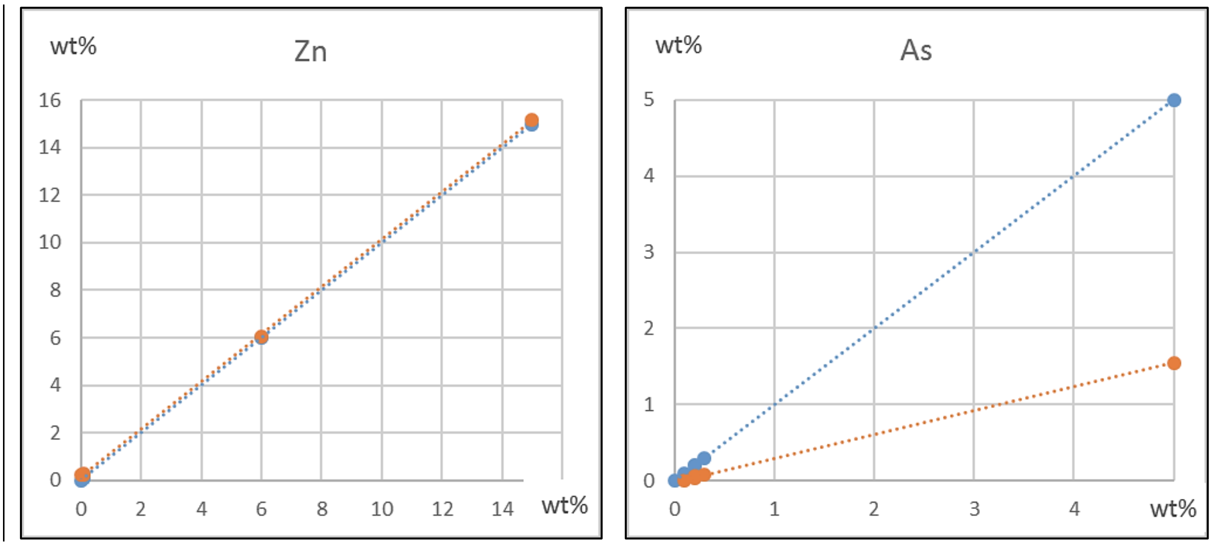


Fig. 5.7: Deviations of the measured results (orange dots) plotted against the values of the IMMACO reference alloys (blue dots), for the elements copper, lead, antimony, zinc, tin and arsenic.

The numeric results for the main elements besides the copper, i.e. Pb, Sb, Zn and Sn, are very close to the values of the IMMACO standards (see Fig. 5.7). However, for arsenic (As) there is an important under-estimation of the values present. This deviation was also noted by other researchers while testing the applicability of handheld portable XRF for the characterisation of archaeological copper alloys (Nicholas & Manti, 2014). As a conclusion from these results, an averaged mathematic correction of a factor 3.75 was applied to all As results in the copper alloy compositions presented in this research. Concerning the results on the Cu values, the deviation for alloy 2.7.54 giving 96.8 wt% instead of 93.4 wt% (reference Cu wt%) is therefore related to the bespoke deviation of As. When applying the correction factor, the balance for Cu comes to 92.5 wt%. It can therefore be concluded that the instrument and the software used is capable of measuring copper alloys to a high standard of reliability, qualitative and quantitative results.

5.4.2 Phase 1

5.4.2.1 Results of the measurement on strikes MA 120 etc. and matrices set MA 71

The measurements show, with a very few exceptions, that he matrices sets 'MA 120 etc.', consist of very similar copper alloys, namely a main group (A) of very high purity copper (about 99.5 wt%) with only measurable amounts of lead (Pb, average 0.26 wt%) and antimony (Sb, average 0.23 wt%) (Fig. 5.8). A second group, with a much smaller number of matrices, shows average values for Pb at 0.27 wt% average and elevated concentrations of Sb at 0.44 wt% average (group B). Examples of a copper alloy with approx. 0.5 wt% of Pb and Sb are presented in Fig. 5.10, where it can be seen that lead is distributed in the copper-antimony bulk alloy as separate globules.

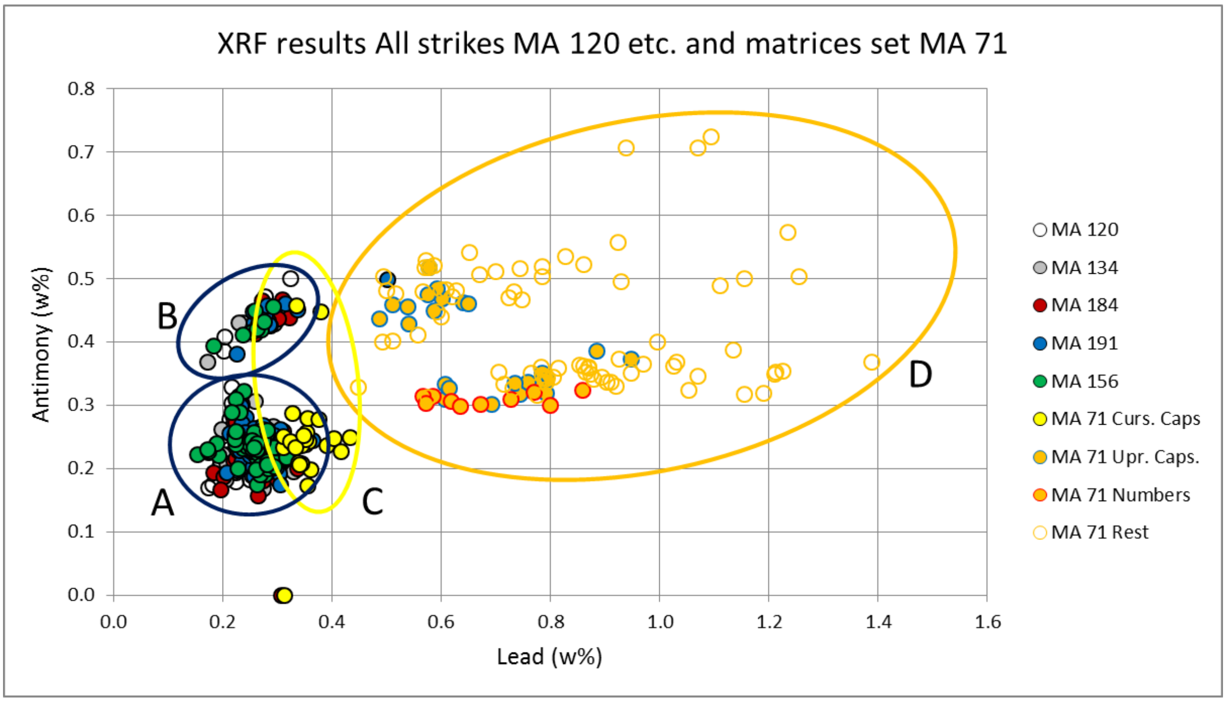


Fig. 5.8: The registration of all measurements shows the grouping of all sets of strikes (blue groups, A, B) and group D (orange) representing matrices set MA 71. The cursive capitals in set MA 71 are a separate group (yellow, C)

In this group B with an antimony content exceeding 0.35 wt%, it is worth noting that the matrices for the lower cases *c* and *e* are repeatedly situated in this group. Also, several numbers and some accents belong to this specific group, throughout the different matrices sets (Fig. 5.9). This could point to the fact that Granjon had access to two batches of copper rods. It is difficult to establish why it was chosen to make the matrices of *c*, *e*, and some numbers and accents in copper from a different batch; it may just be a coincidence. Nonetheless, it shows that the matrices were probably struck with the respective punches consecutively in the same copper rods. Finally, the 0 (zero) from strike set MA 184 contains no antimony at all, which is an exception to all the results. (Fig. 5.9) The external visual aspects are no different from the other strikes.

Matrices set MA 71 is not similar in composition to any of the other measured sets, except for the cursive capitals (Fig. 5.8). These cursive capitals (25 matrices, top left in box) are a separate group from the other alloys within MA 71. The copper alloy is also relatively pure and homogeneous as a group, with average levels of 0.35 wt% Pb and 0.24 wt% Sb. Within this group there are three exceptions: the matrices E and V have a high level of Sb (0.45 wt%), while the matrix U has no Sb. For the latter, this almost certainly points to an addition of the matrix. (Fig. 5.9)

The close match between the results for the cursive capitals in MA 71 and the other sets (MA 120, 134, 156, 184 or 191) and the fact that two of the matrices also have an elevated Sb content, raises the possibility that Granjon also produced these strikes. Since MA 156 does not contain the capitals (any more), it can be assumed that these were used to be justified and to complete the MA 71 set. The measurements tend to show this, including two deviated letters (E,V) with a similarly higher Sb content as seen in the other matrices sets. However, there are two remarks to be made. Firstly, there is a slight deviation in Pb content, which is probably due to the segregation effects that are eliminated in this set by justifying the matrices. From the results it could be concluded that the minimal removal of material for smoothing the strike surface of the non-justified matrices is not able to prevent the segregation effects from the casting. If this assumption is correct, the actual Pb content in the matrices' bulk copper could be somewhat higher, as the results of group C indicate. Secondly, as with the other strikes, none of the capitals have an elevated concentration of antimony, which contests the likelihood that these were harvested from MA 156. But, since only 5 of the original 11 sets were measured, there is room for speculation.

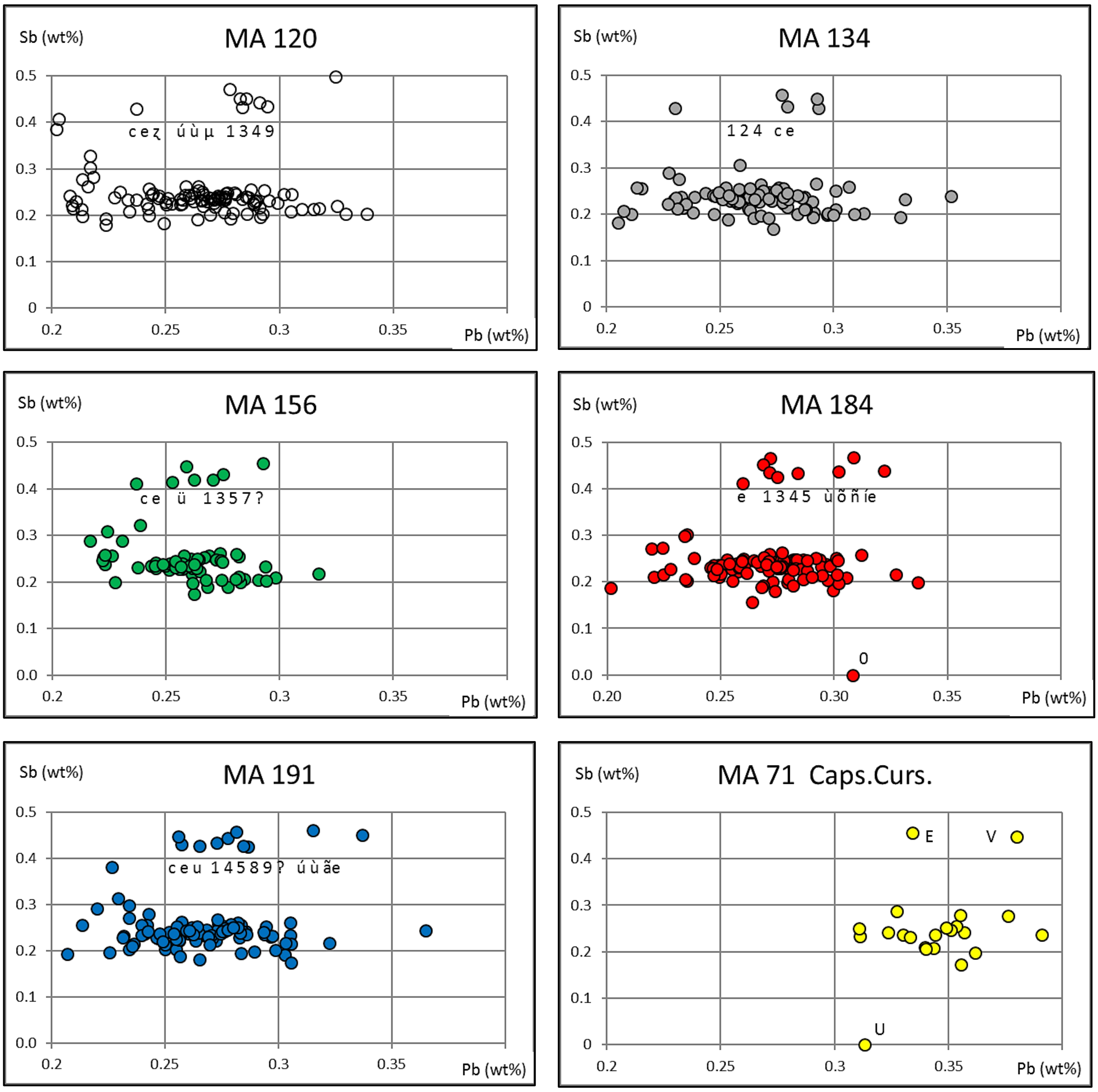


Fig. 5.9: All individual matrices XRF results on each of the sets of matrices denoted as 'MA 120 etc.', completed with the sloping capitals in MA 71 (Caps.Curs.).

None of the other alloys in set MA 71 correspond to the matrices sets of Jolie Cursive. The average values of the very dispersed measurements are 0.78 wt% Pb (0.45-1.39 wt%) and 0.41 wt% Sb (0.30-0.72 wt%), see group D in Fig. 5.8. In the same graph we notice that the numbers, which are struck from another set of punches, form a relatively dense group at least at the level of Sb content.

However, these alloy compositions appear equally in other matrices of MA 71. Also, the upright capitals resemble the copper composition of the other (non-cursive capitals) matrices.

The results show that XRF has the ability to measure small differences in adjacent metals present in copper. The most significant elements that seem to be present in these 16th century matrices are lead and antimony. The presence of lead globules throughout the copper is shown in Fig. 5.10. The analytical result of this SEM-EDX measurement is: Cu 98.8 wt%, Sb 0.5 wt%, Pb 0.7 wt% (Livetime 30 s). Antimony on the other hand is dissolved in the copper, as a spot analysis on a lead globule reads Cu 27.8 wt%, Sb 0.6 t%, Pb 71.6 wt% while a spot analysis on the Cu-Sb matrix gives Cu 99.7 wt%, Sb 0.1 wt%, Pb 0.2 wt% (Livetime 300s). Other elements such as iron and silver may be present, but are too close or below the detection limit of the instrument and therefore not considered here.

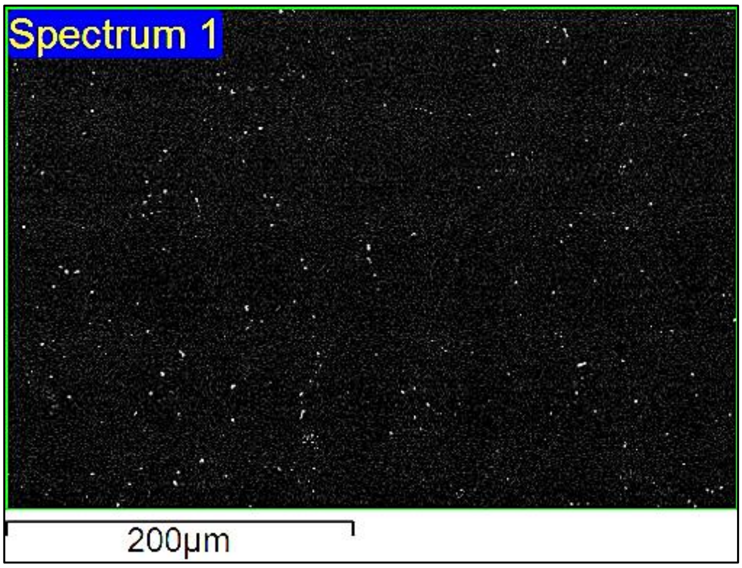


Fig. 5.10: SEM-EDX of a 400 x 300 µm area on a copper alloy with 0.5 wt% of Pb and Sb each. White spots indicate the distribution of the lead globules.

5.4.2.2 Case study 1

As a first case study, the selection of the matrices set MA 76 was made according to the supposition in the 1960 Parker & Melis Inventory that the Roman capitals could have been moved from MA 71 to MA 76. The revised comments on this set, published in De Gulden Passer 1960 (p.62), have already abandoned this idea for the following reasons: “Plantin may have bought these matrices since they are not listed in the *post* 1581 De Vechter Inventory. However, the first inventory to list a second set of *Jolie Romaine* matrices seems to be the 1652 Inventory, which is somewhat confused in the smaller sizes. MA 76 is equipped with the small capitals to Van den Keere’s *Coronelle* instead of the capitals of the *Jolie*. There are two plausible reasons for this: either Van den Keere had not cut the *Jolie* capitals when he made this strike and so substituted the small capitals from the earlier *Coronelle* (see ST 21) or else the set is a late one and the change in capitals is due to confusion.”

The XRF results for the Pb/Sb ratios of each matrix in the set are shown in Fig. 5.11. From the total of 126 matrices, 110 appear to contain no antimony (majority in red dotted circle, where the , à and [show a higher lead value), 10 results with a low antimony/high lead content and 5 matrices with a very high antimony/low lead concentration. All results that deviate from the main group are accents. The only two exceptions on the described groups are the lower case letters m and s.

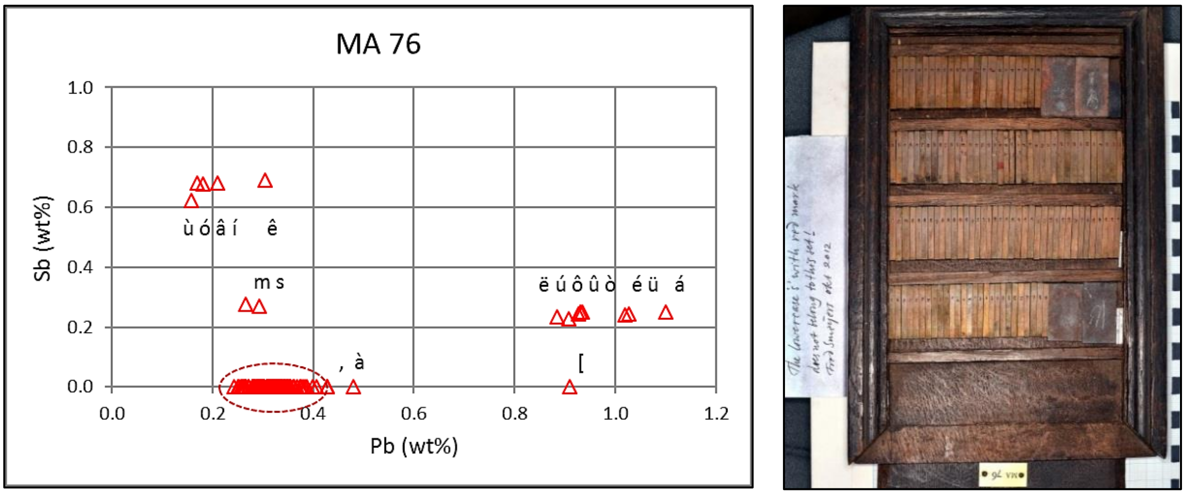


Fig. 5.11: XRF results for Pb and Sb on 126 matrices (left graph) from set MA 76 (right photograph).

The small capitals, which are thought to have been moved from this set to MA 76, do not resemble any composition found in MA 71. All capitals in MA 76 have a composition with a low concentration of lead (c. 0.30 wt%) and no antimony, which is remarkable. The capitals also match the rest of the set, i.e. lower cases (except for the m and the s), the ligatures, the numbers and punctuation (except for [) and most of the accents. The latter group however shows two other sub-groups, but none of them with a composition that can to be related to MA 71. In conclusion, it appears that this set is consistent as a whole in its alloy compositions, except the m and s and a number of accents, which are struck in two deviant kinds of copper rods. It is worth mentioning that in 2012 Mr. Fred Smeijers added a note to the matrices' box, saying that the lower case 's' does not belong to this set. This is supported by the XRF result, but it also indicates that perhaps the letter 'm' should be checked as well.

A matching set to MA 76 is MA 70, also Jolie Romaine and equally attributed to Van den Keere. The compositions of MA 70 matrices (see Appendix) match very well other matrices from Van den Keere, as will be seen later in this chapter. It remains therefore a question why Plantin had two comparable sets and where MA 76 could find its origin. Based on the measurements that were executed in Phase 2, the composition of copper without any antimony in MA 76 would point towards Le Bé. There is however no other evidence at this point to state this hypothesis.

5.4.2.3 Case study 2

As a second case study, matrices set MA 58 attracted attention because of the yellowish appearance of some of the matrices (Fig. 5.12). The set consists of Caps, lc, lig, acc, nos, punct, 150 matrices (Parker-Melis Inventory, 1960). The Inventory further comments: 'In 1561, Plantin had matrices for a 'Breviaire Italique' [Inv 1561]. On January 1st 1562 he received from 'Francoijs le Fondeur' matrices for 'Italica Brevier N° 153', which he sent off to Martin le Jeune in Paris [Arch. N° 54; 36 p 17v°] probably as a precautionary measure before his own flight. The 1563, 1572, 1581 and Antwerp 1589 Inventories all list a set of Breviere or Bible Cursive matrices by Granjon, the latter giving the number as 157. The c. 1612 Octavo Inventory and the 1652 Inventory list 157 Bijbel Cursive. In October 1572 Van den Keere revised all the matrices of the 'Cursive de breviere' and replaced a missing comma [Arch. 153 p 150]. On January 4th 1576 he charged Plantin for adding an ñ to the 'bible Cursive' [Arch. 153 p 183] which is in this set.'

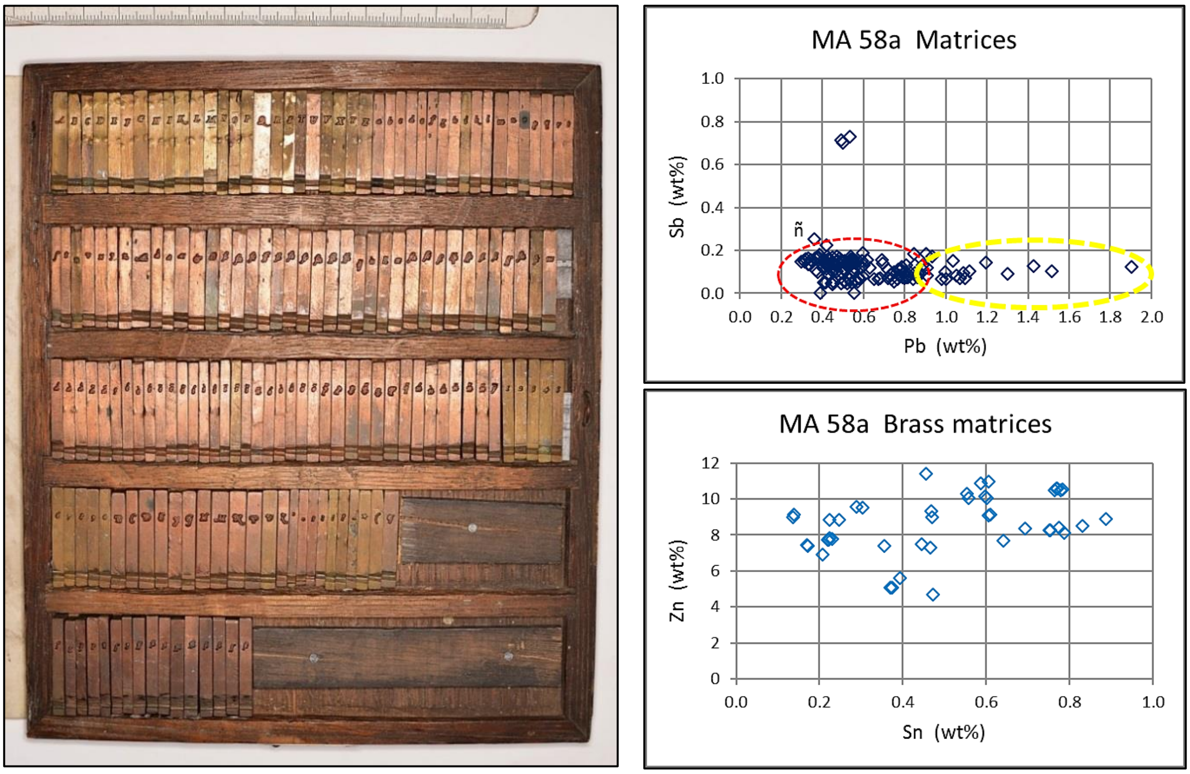


Fig. 5.12: Left, the visual appearance of the set MA 58a-b. On the right the XRF results with in the top graph the elements Pb-Sb and in the lower graph Sn-Zn for the brass matrices in the set. Copper matrices in the top graph are indicated by the red circle, brass matrices are in the yellow circle.

The yellowish and red appearance of the matrices proved to be a mix of brass and copper, as shown by the XRF results in the two graphs on the right. The brass also contains, besides the zinc(Zn) content (average 9 wt%), a very small and varying amount of tin (Sn, average 0.5 wt%) in its alloy composition (lower graph). The brass also has an elevated concentration of lead, indicated by the yellow circle (upper graph); the copper matrices are situated in the red circle, except for the capital U, the additional capital F (denoted ‘F) and the punctuation mark. The ñ, which is added by Van den Keere, in 1576 is situated at the outer edge of the main group’s composition. The lead-antimony content in the brass matrices is situated within the yellow circle.

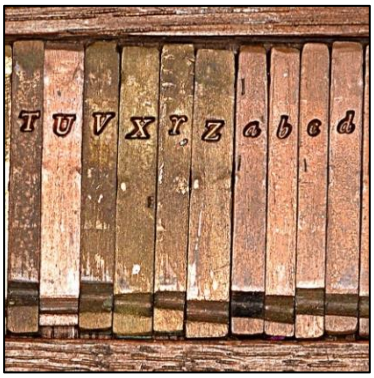


Fig. 5.13: Brass capitals T V X Y Z and copper matrices U, a-d.

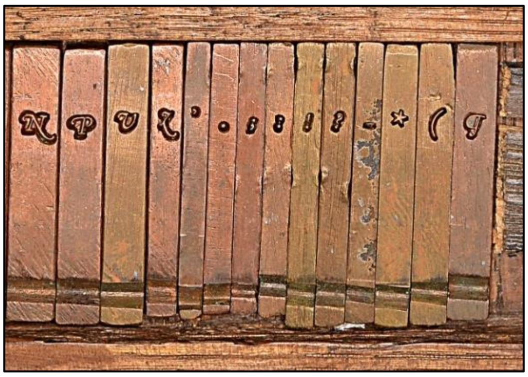


Fig. 5.14: The additional capital V in brass, followed by the punctuations in brass: ! ? - * (, other matrices in copper, no comma.

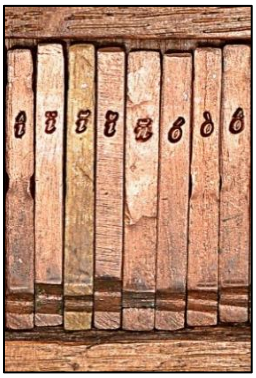


Fig. 5.15: Detail of the brass ĩ and the added ñ in copper.

All the capitals (except U, Fig. 5.13) are struck in brass of about 9 wt% zinc and averages of 0.5 wt% tin and 1 wt% lead. Other matrices in brass are: i, u, ʃt, ı̃, the additional capital V, punctuations :, !, ?, -, * ((Fig. 5.14).and all the numbers 1, 2, 3,…, 0.

The comma, previously mentioned as being replaced by Van den Keere in 1572, is not in the set today. The additional ñ by Van den Keere in 1576 is still in the set (Fig. 5.15), its composition slightly deviating from the group of other copper matrices in the set. This set of matrices shows that it is quite possible to use brass for striking matrices, certainly for the smaller typefaces where not too much force is required to drive the punches into the metal. Brass is only slightly harder than pure copper but has the advantage of hardening less locally at the face of the punch. From a metal worker's point of view, it is surprising to see that brass was not used more frequently for the production of matrices, as hardness cannot have been an argument. The lower corrosion resistance or the wear and tear by casting type could, however, be significant reasons to persist in using 'pure' copper.

5.4.2.4 Multivariate data analyses

In addition to the previous analyses, where groups of matrices were observed by plotting metal compositions in a pairwise manner (Pb/Sb and Zn/Sn), multivariate data analyses were performed. These techniques allow for the exploration of patterns in the alloy compositions using the concentration of all 8 measured metals besides copper simultaneously (Pb, Sb, Zn, Sn, Ag, Fe, Ni, As), and showing the extent to which the overall metal composition differs between and within sets of matrices. Some multivariate analysis techniques use the information on group membership to optimally split the observations (here: the matrices) between groups (here: the sets), whereas other techniques ignore the set membership and merely use the observed metal concentrations.

Cluster analysis belongs to this latter group of techniques (Kaufman & Rousseeuw, 1990). In brief, it explores which of the individual matrices are similar across all 8 metals, grouping the similar matrices together in clusters. The actual group (here: set) membership is not taken into account – matrices are assigned to clusters regardless of the set they belong to. The cluster analysis was carried out using the statistical software package R, version 3.4.0 (R-Core-Team, 2014) and the add-on package cluster (Maechler, Rousseeuw, Struyf, Hubert, & Hornik, 2014).

In a first stage, we explored how many clusters would give an optimal separation of the clusters. We pre-specified the number of clusters to all values from 2 to 15 clusters, and plotted the within-cluster versus the number of clusters (Fig. 5.16). This showed that any solution between 5-9 clusters would be acceptable. Table 5.2 shows the results for 7 cluster centres. This was found to correlate optimally with the historical information.

Subsequently, we applied the Partitioning Around Medoids (PAM) algorithm to assign the matrices to the 7 clusters. This is an iterative algorithm, whereby 7 initial cluster centres were defined (in 8 dimensions, for the 8 initial variables). Each observation was assigned to the nearest of the 7 initial cluster centres. Therefore, 7 new cluster centres were calculated based upon the observations belonging to one cluster. Typically, cluster centres shift with regard to the initial cluster centre. Using the novel cluster centres, individual observations were again assigned to the nearest cluster centre. This algorithm was repeated iteratively until the cluster centres no longer changed. The final solution assigned each observation to one of the 7 clusters.

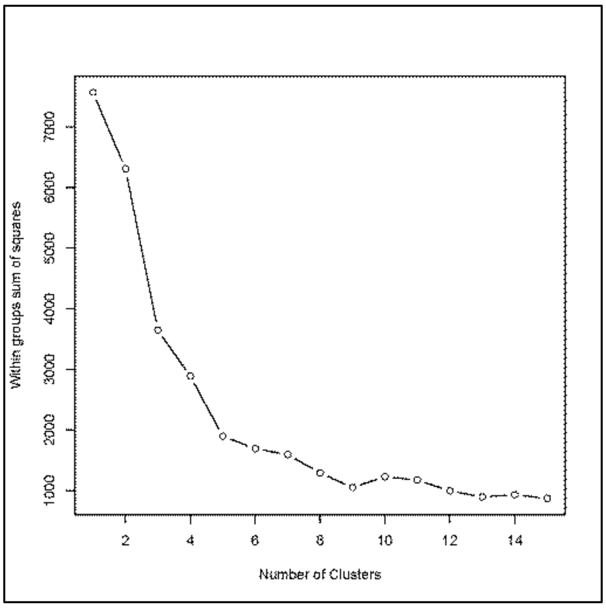


Fig. 5.16: Variability within clusters (y-axis) versus Number of Clusters (x-axis).

In table 2, cluster membership is plotted versus set membership. Almost all matrices from set MA 120, 134, 156, 184 and 191 belong to one and the same cluster, indicating that their composition is similar. Also, the cursive capitals of MA 71 are attributed to this cluster, supporting the previous observations. On the other hand, MA 58a consist of matrices that are mainly assigned to 3 other clusters, indicating that this set was not put together at the same time or from the same batch of copper. In detail, the lower case letters belong to cluster 2, while the ligatures are assigned to cluster 5 and the brass matrices are in cluster 6. It is also interesting to see that the letter ñ, added later by Van den Keere, is separated from the others by its position in cluster 1. MA 58b on the contrary is totally assigned to cluster 7, which consists almost exclusively of matrices from this set, and conversely all matrices from set MA 58b are assigned to cluster 7, highlighting that this matrix set is distinct from the other sets. Finally, the matrices, except for the cursive capitals in MA 71 and MA 76, are all distinguishable from the measured sets.

Table 5.2: Cluster analysis giving seven distinct groups for each set and its individual matrices.

	Cluster assignment						
	1	**2**	**3**	**4**	**5**	**6**	**7**
MA120	110	0	1	0	0	0	0
MA134	111	0	0	0	0	0	0
MA156	77	0	0	0	0	0	0
MA184	110	0	0	1	0	0	0
MA191	110	0	1	0	0	0	0
MA58	1	79	3	0	22	44	1
MA58B	0	0	0	0	0	0	16
MA71	28	2	105	0	0	0	0
MA76	2	4	1	110	8	0	0

5.4.2.5 Discussion

With this measuring technique, we were able to show that certain strikes and matrices were made either from a same batch of copper or from different groups of copper alloys, including also a minority of brass matrices. These observations also show the level of measurement accuracy, since the separation of the groups cannot be seen as a coincidence. Simultaneously, a certain deviation of results within each group cannot be avoided because of the metal alloy itself, segregation effects, possible corrosion layers or other substances on the surface, the fact that XRF is a surface measuring technique and because the peaks for the accompanying elements besides copper in the spectrum are relatively weak as a signal-to-noise ratio. The maximum overall deviation on identical materials with the measurement settings as described lies at around 0.1 wt% (+/-). From these first measurements, we can make preliminary assumptions concerning the average levels of lead and antimony contents in 'pure' copper in the 16th century. This is supported by measurements on '*insculpatieplaten'* or copper plates carrying the punch marks of goldsmiths from the 16th century.[2] Very similar levels of lead (average of 0.6 wt%) and antimony (average of 0.3 wt%) were found in these plates, which were also used as pure copper for a similar goal, i.e. the registration of goldsmith's punch marks. As for the composition of matrices, many more measurements are needed to increase the critical mass for statistical evidence. Nevertheless, this measuring technique can be considered a useful tool for determining groups in historical metal objects.

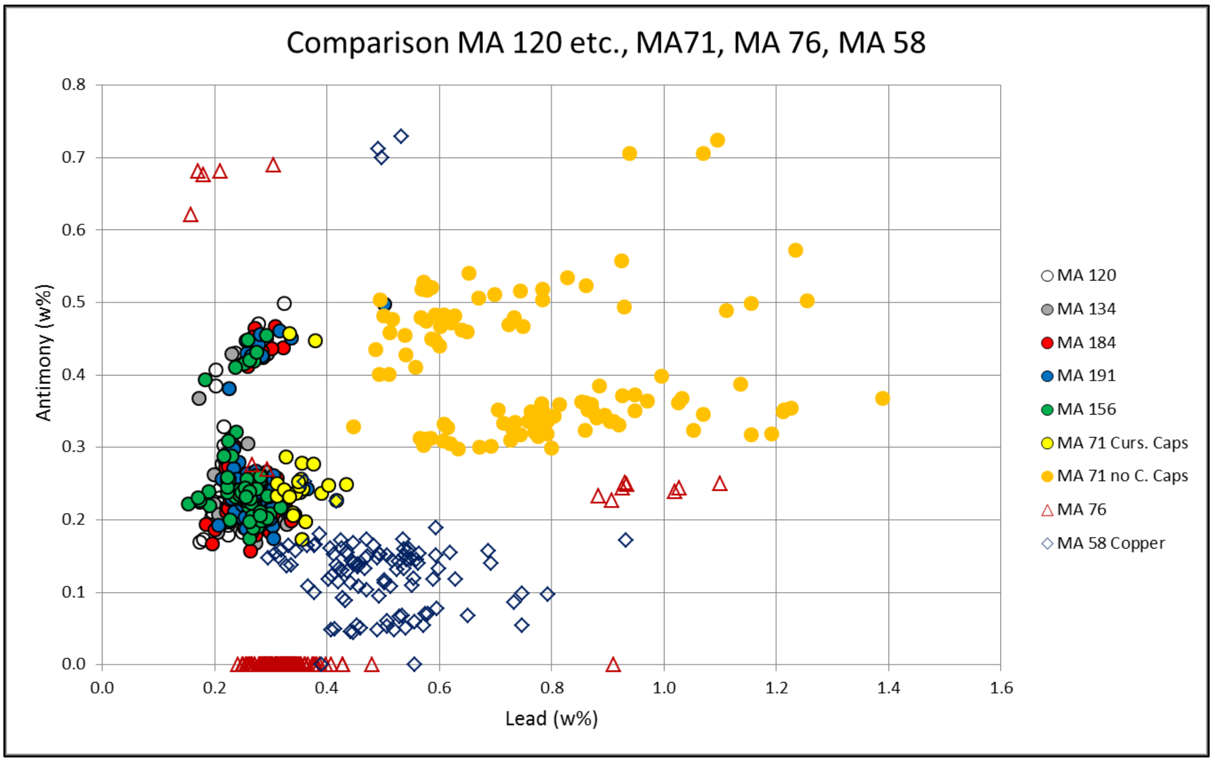


Fig. 5.17: Comparison of all XRF measurements in Phase 1 (Pb and Sb ratios), showing the grouping per set and the parting of non-matching sets and/or matrices.

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[2] Copper plates from the collection of STAM, Ghent (XRF measurements by the author, not published)

When comparing the measured sets of matrices, the grouping of identical sets and the separation of non-matching sets is evident (Fig. 5.17). The very close concentration of the strikes MA 120 etc. with its two groups of copper as described above, including the very close match with the sloping capitals from MA 71, can be observed. The results of the other matrices in MA 71 show a relatively large spread of lead concentration results, but also give two levels of antimony concentration. Set MA 58a is made of copper with noticeably lower concentrations of lead and antimony as far as the copper matrices are concerned, whilst set MA 76 is isolated from the other sets because of the absence of antimony for 110 out of 122 matrices. The few matrices with deviated concentrations of lead and with antimony are also clustered in two groups, separate from the other results.

From the archives and the inventories, it is unclear exactly when MA 71 was made or when it was changed or completed. If this set is '*Les matrices de granjon cursive nonpareille*', it was bought by Plantin in 1573 from Granjon [Arch. Inv. 116 p. 285]. The XRF results simply show that the sloping capitals are a separate group in the set and that the compositions very closely match these of the sets of strikes 120 etc. The other matrices in the set do not show distinct groups apart from the two levels of antimony content. Therefore, it is likely that all the matrices in MA 71 (except for the sloping capitals) were produced from the same copper supply. Additionally, it can be noted that the upright capital compositions are part of both groups of antimony content, whilst the numbers are exclusively and well grouped at the lower antimony level (Fig. 5.8).

MA 76 with the punches ST 22 is attributed to Van den Keere, 1575. This set would have been bought by Plantin upon Van den Keere's death in 1580. The only other mention of a second set of Jolie Romaine matrices seems to be in the 1652 Inventory which lists '129 Jolie Romaine, ghejusteert' (Parker & Melis, 1960). They comment further on this: 'It seems reasonable to suppose that Van den Keere's set of matrices might have been struck before he had finished, or started, the correct capitals, and so been equipped with the small capitals from his earlier Coronelle. Alternately, perhaps it postdates 1612 and the capitals are those of MA 71.' The measurement results give no indication of the completion of the set with capitals from another set, certainly not from MA 71. If the small capitals were transferred from Van den Keere's earlier Coronelle, it cannot be excluded that the same batches of copper present in his studio were also used. This would give no different analytical readings. In any case, it seems correct that the assumption of a transfer from MA 71 to MA 76 was abandoned (Parker, Melis & Vervliet, 1960). It would however be interesting to measure Van den Keere's earlier Coronelle (ST 21, MA 161, MA 62, MA 148 strikes) to look at possible material similarities. The complete absence of antimony in the copper is certainly special and points towards 'rosette' or 'rose' copper, as described by Biringuccio and Moxon.

Concerning the set MA 58a, we assume that this is the 'Breviaire Italique' [Inv 1561], attributed to Granjon, meaning it would predate this year. The copper matrices in this set are all low in lead (average of 0.5 wt%) and very low in antimony (average of 0.1 wt%). Of particular interest are the brass matrices. There is no telling whether they were struck at the same time or added to the set to replace missing items, or vice versa for the copper matrices. In addition this, it can be noted that the ñ added by Van den Keere in 1576 is situated at the outer edge of the copper groups composition, showing a low lead (0.36 wt%) and a higher antimony content (0.25 wt%).

Considering that the copper used by Van den Keere in 1576 has a low lead and medium antimony content, we can come back to the MA 76 matrices composition. From there, it is open to discussion whether MA 76 is indeed from his hand. Perhaps MA 76 does postdate 1612 (see above), although the capitals seem not to be from MA 71 and they do match the compositions of the other matrices in the set, suggesting that they were struck from the same batch of copper.

5.4.3 Phase 2

5.4.3.1 Selection of matrices from archival documents

The selection methodology is explained and listed in 5.3.2. From this list, a number of punchcutters/ matrix-makers came forward, such as Hendrik van den Keere, Guillaume Le Bé, etc. The following parts show the analytical results on matrices that are very probably from their respective hands, considering the archival documents in the MPM.

5.4.3.1.1 Hendrik van den Keere

The matrices would date from between 1569-1580. The selected matrices sets or individual additions (denoted * with the matrix set number) are: MA 1ab, 4, 21*, 25a*, 48ab*, 54a*, 54b*, 58a*, 62, 67*, 68, 70, 78, 82a, 91ab, 92de, 93, 96, 102, 142*, 160*, 161.

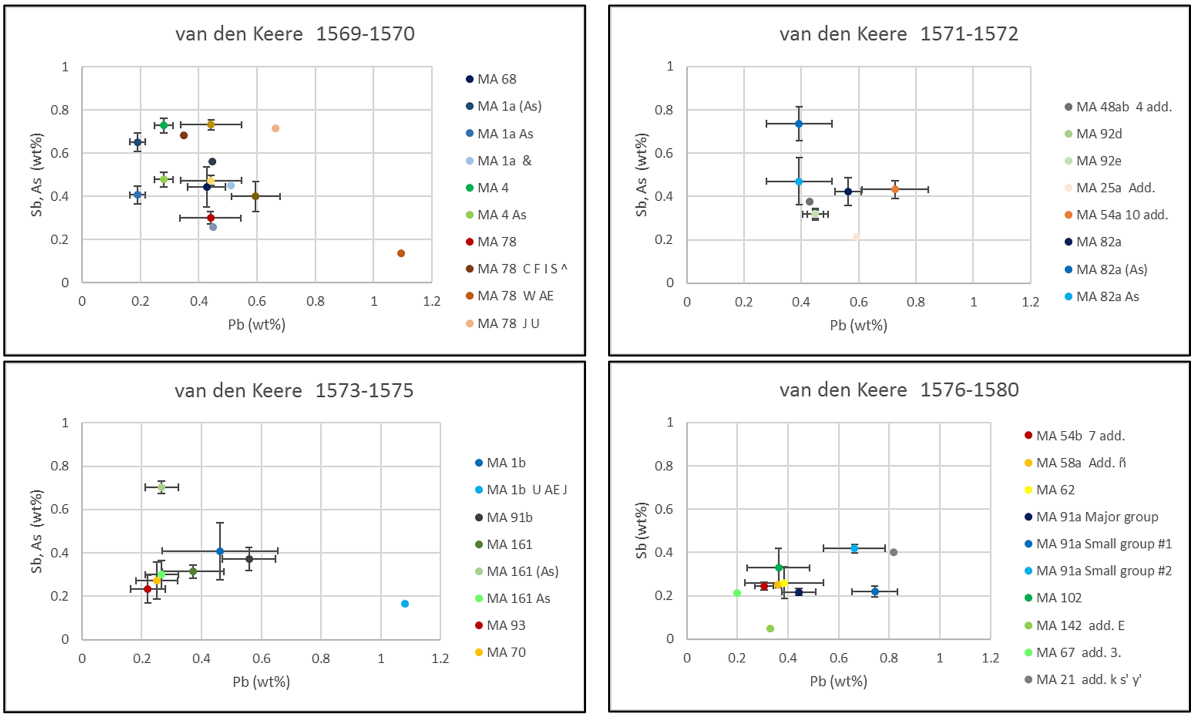

Fig. 5.18: XRF measured compositions of matrices by Hendrik van den Keere, divided into four periods of his active working years: 1569-1570, 1571-1572, 1573-1575 and 1576-1580.

Van den Keere seems to have used mainly two kinds of copper, namely with and without arsenic (As). Looking at the Pb/Sb content in the coppers he used, the results show that the overall Pb content lies between 0.2 and 0.6 wt% for all years, whilst the Sb content varies greatly between 0.2 and 0.8 wt% in the earlier years, decreasing in later years to levels between 0.2 and 0.4 wt%. For the arsenic-containing coppers that he appeared to use only in his earlier years, i.e. until about 1573 at the latest (date of justifying set MA 161) and for which an overview of the Cu/As alloys is given in Fig. 5.19, it the

Pb level is between 0.2 and 0.5 wt% with a relatively even level of Sb at 0.3 and 0.5 wt%. The As content lies between 0.6 and 0.8 wt% although the remark on the measuring of As levels with XRF should be kept in mind (see 5.4.1). The graph in Fig. 5.19 shows similar variations in concentrations of Sb compared to the As. Because of this and because of the possible Pb segregation issue as described in 5.4.2.1, there is a question as to whether this could have been the same copper that Van den Keere used. Further investigations are needed to clarify this.

The copper matrices containing As (Fig. 5.19) show considerably higher concentrations of Sb (about 0.7 wt%), compared to the matrices without As (Fig. 5.20). This group of matrices also show levels of Pb between 0.2 and 0.6 wt% with Sb contents between 0.20 and 0.45 wt% as average values per set.

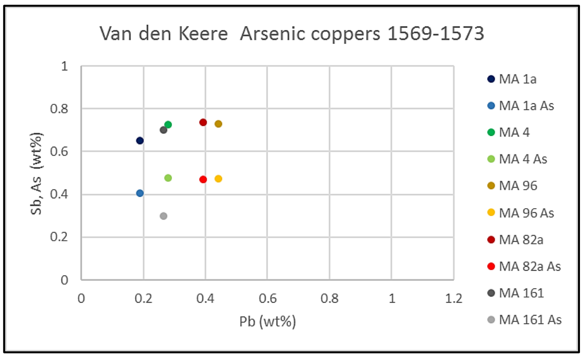

Fig. 5.19: XRF on arsenic-containing matrices by Van den Keere, Pb-Sb and Pb-As ratios.

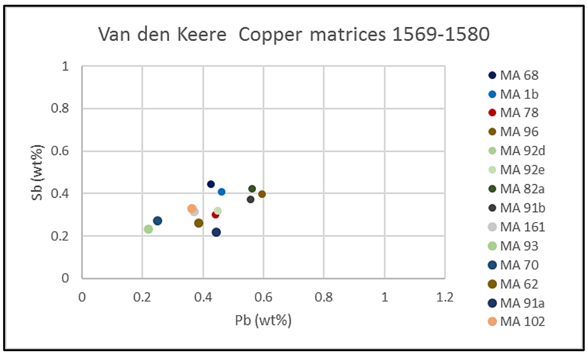

Fig. 5.20: Overview for Pb-Sb ratios in As-free matrices by Van den Keere in his active period.

5.4.3.1.2 Guillaume Le Bé I

The matrices made by Le Bé would date from 1551-1573. The selected matrices sets are: MA 6, 40, 47a, 72, 97. These are all complete sets and there are no additions to other sets known to have been completed by Le Bé.

All the XRF results on matrices of Le Bé (Fig. 5.21) show a number of matrices with no or very low Sb, and a group with moderate Sb levels (0.3-0.4 wt%). There is one deviant set, being a small group of matrices from MA 72. A detail of the results from the matrices with no or very low Sb concentrations (Fig. 5.22) show two groups that are identical (MA 72, MA 6) and 3 groups that are very similar, possibly produced from the same copper batch (MA 6, 40, 47a).

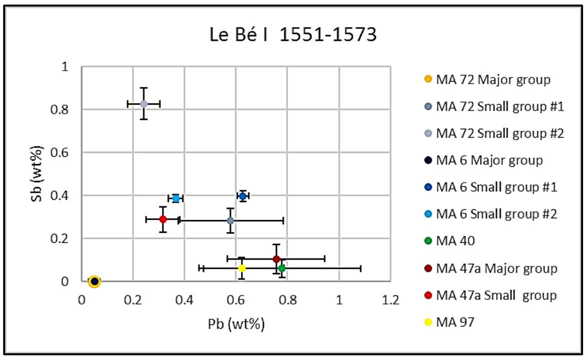

Fig. 5.21: XRF results for Pb and Sb on all measured matrices from Le Bé.

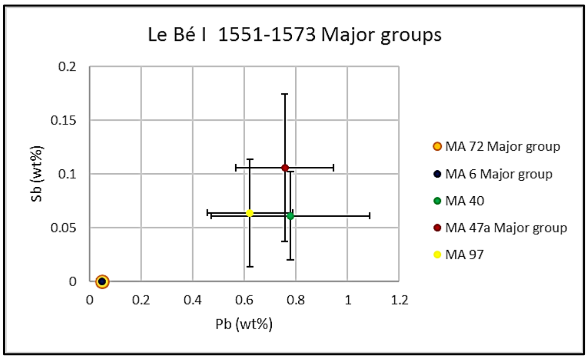

Fig. 5.22: Detail of Fig. 5.21, below 0.2 wt% Sb.

The most remarkable result is that MA 6 and MA 72 are identical to each other. This does comply with historical facts that MA 72 is from Le Bé's Hebrew N°9 cut in 1551 and used by Plantin from 1564. The other set, MA 6, is the Hebrew N°10, cut in 1559 and used by Plantin also from 1564. A strong hypothesis can therefore be that Le Bé struck these two sets at the same time, as an order from Plantin, and sold them together with the punches ST50 to Plantin in 1562 (Parker & Melis, 1960). Furthermore, both sets have averages values of Pb/Sb 0.05/0.00 wt% (±0.05/0.00) and are the purest copper alloys in the entire collection of measured matrices.

The other matrices sets from Le Bé, or at least the major parts of it, have very low Sb concentrations below 0.15 wt% average. It seems that Le Bé chose the purest copper he could find, when working in Paris.

5.4.3.1.3 Robert Granjon

The selected matrices would date from 1545-1574. These sets or individual additions (denoted * with the matrix set number) are: MA 11, 15, 24*, 54a, 118, 119, 120, 121, 122, 128, 134, 156, 182, 183, 184, 191.

The analytical results for all measured sets of matrices show two significant outlined groups and a few sets with very low Sb content (Fig. 5.23). When allocating the results to the assumed years of production, it is noted that in the earliest years Granjon had access to copper with very low Sb content (Fig. 5.24). Also in these years, he seems to have produced MA 15, which is made of brass (copper-zinc alloy) rather than 'pure' copper. (see 5.4.3.3). An exception in the results is noted for the major group of matrices from MA 54a, with a higher Sb content. The results suggest that they may have been produced in Antwerp, since these Pb-Sb concentrations match with matrices produced by Granjon when working in Antwerp.

The matrices sets that are dated 1570 and which were struck to an order of Plantin (MA 11, 118 etc., Fig. 5.25), show identical results with averages of Pb at 0.5 wt% and Sb at 0.4 wt%. Granjon worked in Antwerp from the mid-1560's until 1570. The composition of this copper is comparable to the average compositions of the copper used by Van den Keere. In his later period (1574, Fig. 5.26), when he had left Antwerp for respectively Frankfurt, Paris and Lyon, it appears that he had access to a purer copper with Pb/Sb levels of 0.25 wt% each. It should be added that these 5 sets (MA 120 etc.) were struck to an order of Plantin, who simultaneously bought 11 sets of this face in 1574 (see also 5.4.2.1).

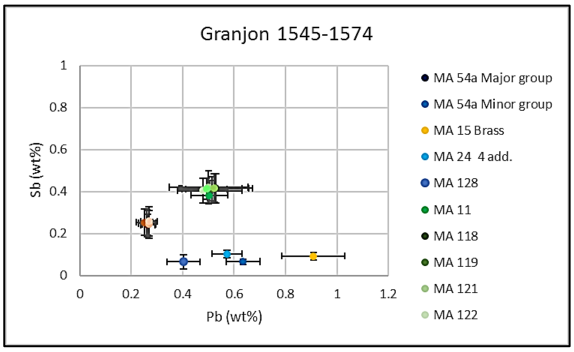

Fig. 5.23: XRF results for matrices by Granjon, throughout his production years.

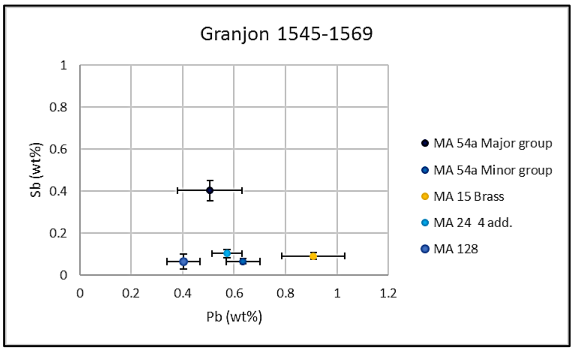

Fig. 5.24: Matrices from the early years of Granjon, before 1570.

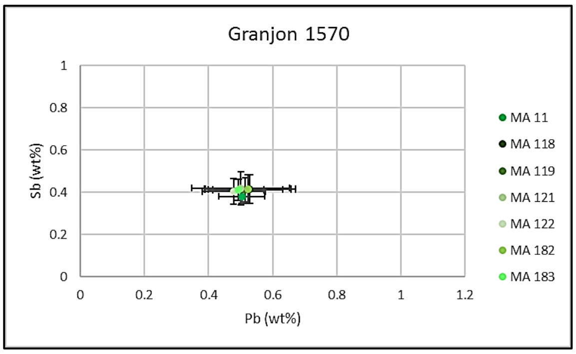

Fig. 5.25: XRF results on MA 11, 'MA 118, etc.'

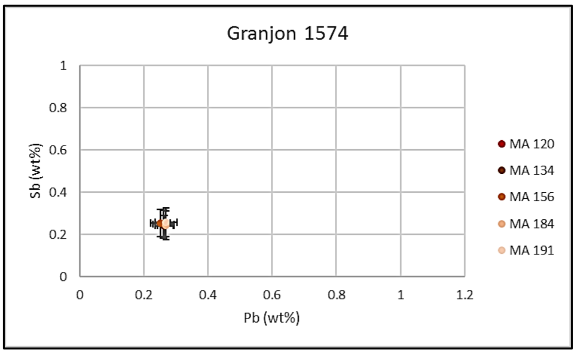

Fig. 5.26: XRF results on sets 'MA 120 etc.'

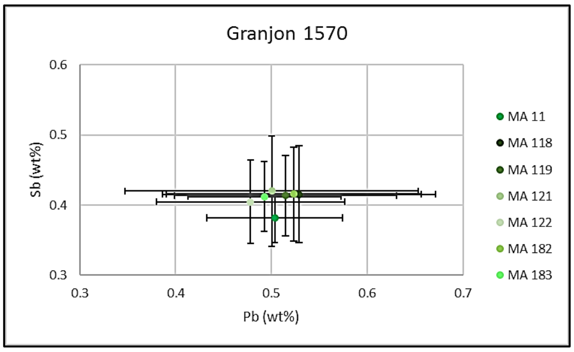

Fig. 5.27: Detail of the results from Fig. 5.25.

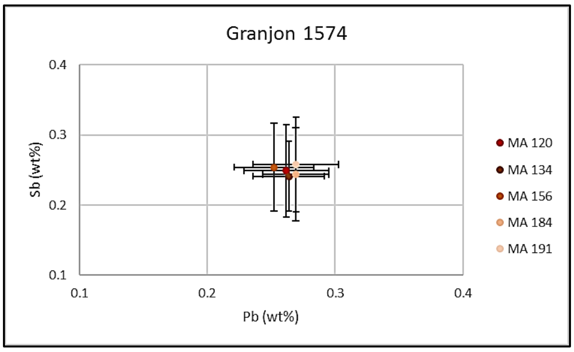

Fig. 5.28: Detail of the results from Fig. 5.26.

5.4.3.1.4 François Guyot

The matrices from Guyot's hand would date from 1562-1567. The selected matrices sets or individual additions (denoted * with the matrix set number) are: MA 34, 56a*, 57. The analytical measurements (Fig. 5.29) show a close group of medium levels of Pb (average 0.6 wt%) and Sb around 0.4 wt%. The addition of the G to MA 56a does not fit in this range.

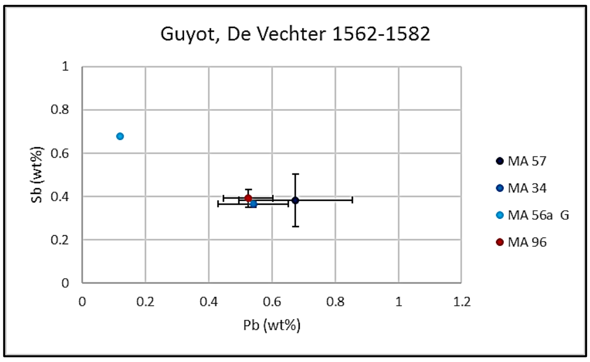

Fig. 5.29: XRF results on matrices by Guyot (MA 34, 57), besides one set by De Vechter (MA 96).

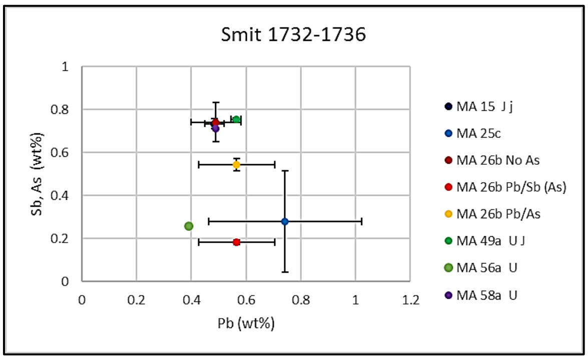

Fig. 5.30: XRF measured copper compositions of sets and added matrices by Smit, 18th century.

5.4.3.1.5 Thomas De Vechter

De Vechter was the foreman in Van den Keere's workshop and continued working after the death of Van den Keere in 1580. The matrices of MA 96 are attributed to him (Fig. 5.29). The copper composition very much resembles the copper of Guyot. This could be explained by the fact that they both worked in Antwerp and could have had the same copper supplier.

5.4.3.1.6 Johan Michael Smit

The matrices would date from 1732-1736. The selected matrices sets or individual additions (denoted * with the matrix set number) are: MA 15*, 25c, 26b, 49a*, 56a*, 58a*. Only two complete sets are measured, besides a number of additions to other sets (Fig. 5.30). There is little coherence in the results; for instance, Smit has used copper with and without As one set (MA 26b). Moreover, it is surprisingly that copper compositions in the 18th century were not more purified and constant in quality. It seems that Smit used whatever copper he could get his hands on.

5.4.3.1.7 Peeter Van Wolsschaten

The matrices would date from 1674-1690. Only individual additions are recorded in the Plantinian archives: MA 48ab*, 57*, 62*. The results show little coherence and not many conclusions can be drawn from them (Fig. 5.31).

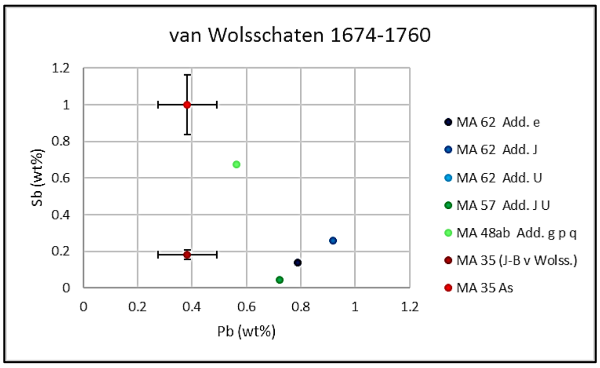

Fig. 5.31: XRF results of additions to sets of matrices by Peeter Van Wolsschaten and MA 35 from Jean-Baptiste Van Wolsschaten, with As.

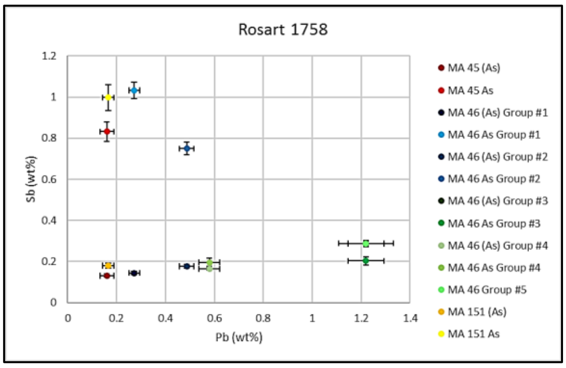

Fig. 5.32: XRF results for the As-containing coppers used by Rosart.

5.4.3.1.8 Jean-Baptiste Van Wolsschaten

The matrices would date from 1760. The selected set of matrices is MA 35, which contains As at approx.. 1 wt% and low Sb, approx. 0.2 wt% (Fig. 5.31).

5.4.3.1.9 Jacques François Rosart

The matrices would date from 1758. The selected matrices sets are: MA 45, 46, 151. Three sets are measured, of which MA 151 is a very small set and assumed to be an apprentice practice piece (Parker & Melis, 1960). However, the other two large sets show a mix of different coppers, all containing As but with varying Pb and comparable Sb concentrations. Overall there are large differences in copper compositions by Rosart, although they all contain arsenic with a concentration around 1 wt%, except for 2 groups in MA 46 that are only 0.2 wt% As. Sb levels are low, as with other 18th century results (Fig. 5.30, Fig. 5.31). The variation in Pb levels is perhaps due to a segregation effect in the copper pieces and the group between 0.2 and 0.5 wt% Pb could in fact be the same copper. This could be investigated further. The note about the quantification of As from the XRF results has to be remembered too (see 5.4.2.1).

5.4.3.2 Selection and comparison of matrices with probable attributions

5.4.3.2.1 Hendrik van den Keere

The matrices MA 3b, 76, 144, 145, 148, 188d,e,h,i,m,n,o in this selection date from 1561-1575.

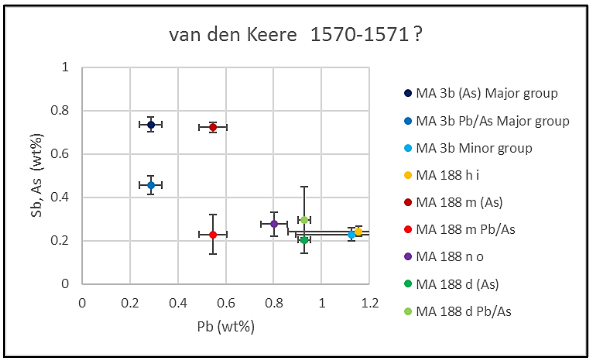

Fig. 5.33: XRf results on matrices and additions in other sets from around 1570 by Van den Keere.

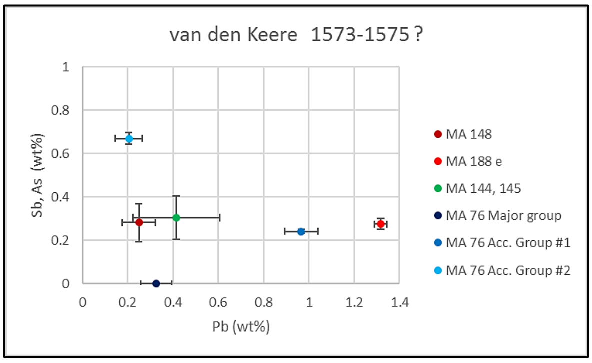

Fig. 5.34: XRF results on copper matrices by Van den Keere, assumed to be from the period 1573-1575.

In the matrices from the period around 1570, a mix of copper with and without As in the composition was measured. MA 3b and MA 188 m seem in line with earlier arsenic copper compositions by Van den Keere (Fig. 5.33). The other set parts deviate from the copper composition that the earlier measurements have shown (Fig. 5.18). For the later period, around 1574, MA 144, 145 and MA 148 correspond to earlier results (Fig. 5.34). In contrast, the major group in the set of matrices MA 76, the two accent groups that were added later to MA 76 and the matrix MA 188e do not match with other results. In the absence of archival evidence, there is no certainty that MA 76 is indeed from Van den Keere’s hand (see also Phase 1). The results would indicate that it is not, and the absence of Sb leads us to Granjon or Le Bé, who both apparently used Sb-free copper quite often.

Concerning MA 188e, Van den Keere sent bills to Plantin for lead casts, but never charged for renting the matrices or sinking the strikes. Also, there is no certainty that this matrix pair of fleurons was struck by him. MA 188i and a minor group of MA 3b show very similar results, just as 188f,g, which are described in the Granjon descriptions below.

5.4.3.2.2 Robert Granjon

The sets of matrices MA 7, 8, 22a, 23, 25b, 26a, 27a, 36b, 47b, 49ab, 51, 52, 53b, 54b, 58a, 63, 71, 101c, 110, 126, 147, 172e, 188fg are attributed between 1560 and 1579. The supposed early copper compositions until 1565, have no or very little Sb content, except for MA 110 and the brass compositions (Fig. 5.35; brass coppers in circle). For the later years when Granjon was in Antwerp, the copper is similar in composition to the metal used by for instance Guyot at that time (Fig. 5.36).

Copper matrices by Granjon show very low Sb concentrations, except for MA 54a its major group. The latter matches his later compositions, as the results of 1570 show. The possibly attributed matrices sets of MA 51, 52 and 53b fit the former results, as they also have very low Sb content. Matrices MA 22a, MA 23 and the copper matrices of MA 172e have extremely low or no Sb. Since it is uncertain that these 3 sets are indeed from Granjon, based on the analytical results, they may have another provenance. On the other hand, it is possible that Granjon used a similar source for his copper to Le Bé, resulting in an absence or at least very low levels of Sb, at less than 0.15 wt%.

For the next period in which Granjon worked in Antwerp (between 1566 and 1570), the Pb/Sb levels in his copper seem comparable to Guyot, with Pb between 0.4 and 0.7 wt% and Sb levels between 0.2 and 0.6 wt% (Fig. 5.36). A few exceptions, namely MA 36b, 47b and 126, have very low Sb values, making them perhaps from the Lyon period. The fleurons MA 188f,g are deviant from the other compositions.

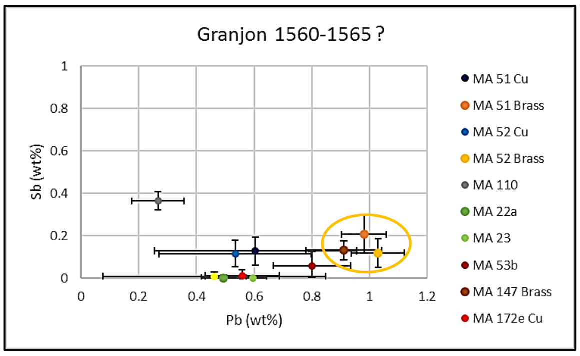

Fig. 5.35: XRF results on matrices by Granjon in his early years, working in Lyon. The yellow circle indicates brass matrices.

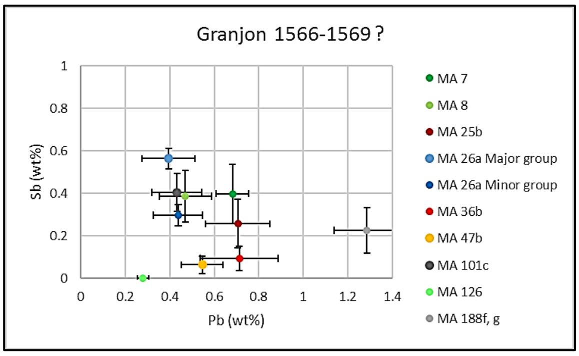

Fig. 5.36: XRF results on the matrices by Granjon, attributed to the years that Granjon worked in Antwerp.

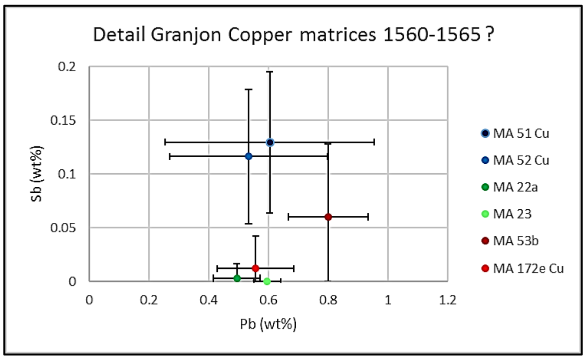

Fig. 5.37: Detail of the coppers with very low Sb content in Fig. 5.35.

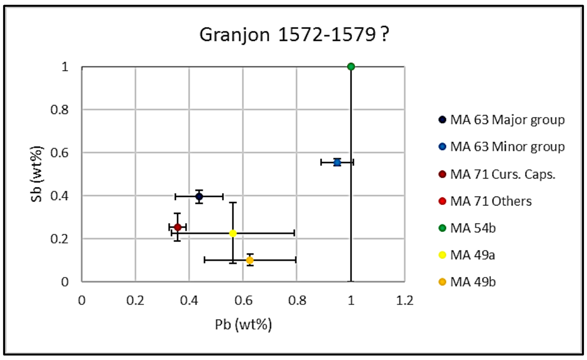

Fig. 5.38: XRF measurements on matrices from the later years of Granjon when he moved from Antwerp through Europe.

In his later years, when he had left Antwerp and travelled through Europe, visiting Frankfurt, Paris, Lyon and finally ending in Rome, some of the analytical results comply with former measurements but some are deviant, as can be seen for MA 54b and a minor group of MA 63 (Fig. 5.38).

It is however important to note that Granjon used brass a number of times. The brass that he used has an average zinc concentration of about 8 wt%, resulting technically in a red brass, also called 'tombac' (Fig. 5.39). Based on the very similar results for both Pb/Sb and Zn/Sn, MA 58a[3] and MA 147 match very well (Fig. 5.40). They also lie within the group reach of MA 15, which the archives suggest is from Granjon. The two adjacent sets MA 51 and 52 are close to the former group, but show slightly higher concentrations for Pb/Sb and lower concentrations for Sn. The Zn and Sn results are also show minor

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[3] For the complementary results on MA 58a, see 5.4.2.3.

deviations. This would mean that they were indeed struck as one whole, but not from the same batch of brass as MA 15, 58a or 147.

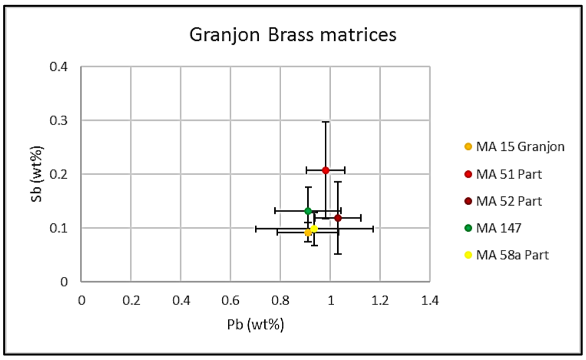

Fig. 5.39: The XRF results with the Pb-Sb levels of brass matrices, possibly by Granjon.

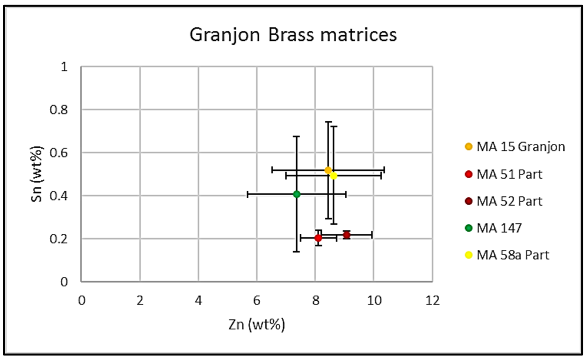

Fig. 5.40: Complying with the Pb-Sb levels (Fig. 5.39), Zn-Sn concentrations.

5.4.3.2.3 François Guyot

The matrices that can be attributed to Guyot are from the years 1555-1567 and are numbered MA 31, 56a, 69, 131b, 153. The analytical results are shown in Fig. 5.41. The results of 56a[4] for the Pb/Sb concentrations are very dispersed and are therefore not taken into account here. The average composition of the copper in the other sets, with Pb approx. 0.5 wt% and Sb approx. 0.35 wt%, complies with earlier measurements of Guyot and others working in Flanders at the time.

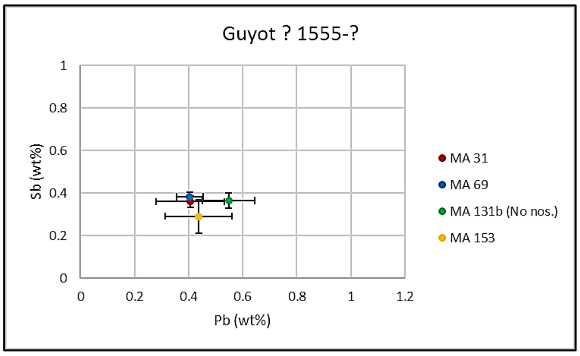

Fig. 5.41: XRF results on copper matrices from four sets, assumed to be by Guyot.

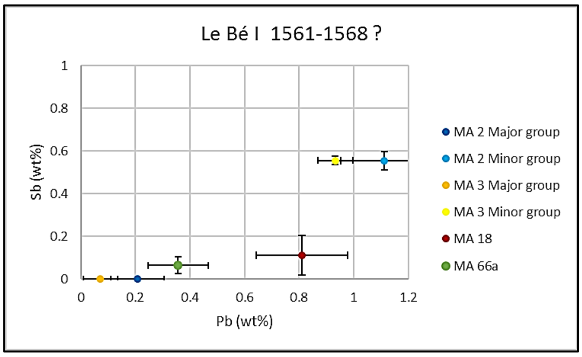

Fig. 5.42: XRF results of sets of matrices, possible produced by Le Bé.

5.4.3.2.4 Guillaume Le Bé I

The sets of matrices MA 2, 3a, 18, 66a (Fig. 5.42) are attributed to Le Bé between 1561 and 1568. The major groups in MA 2 and MA 3 together with MA 66a are a good match with the earlier measurements on Le Bé's matrices, i.e. with very little or no Sb and low Pb values in the copper. MA 18 and the minor groups in MA 2 and MA 3 are however different from all other results from Le Bé until now. It would be necessary to study this in more detail for clarification. All analytical results on the sets of matrices and their groups can be found in the Appendix.

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[4] For detailed results on this set: see the Appendix.

5.4.3.2.5 Claude Garamond

There is a possibility that the matrices 48ab, 59, 60 and fleuron 188l are by Garamond, from 1558 to 1563. The analytical results (Fig. 5.43) for MA 48a show two equally large groups randomly used throughout the set, one with low and one with medium levels of Sb. The set MA 48b has very dispersed results, which makes it difficult to draw any conclusion (see Appendix).

The matrices in MA 59 have a very low Sb content, comparable with the copper that Le Bé and Haultin used, working in Paris. MA 60 also has low Sb, with some matrices slightly higher. The fleuron 188l however contains arsenic, which is therefore not likely to be from Paris, since up to now no measurements with As have to date been linked to this location in this period of time.

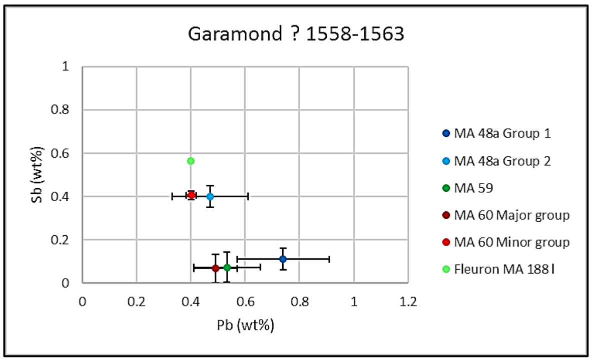

Fig. 5.43: XRF results on matrices, possibly by Garamond, Paris.

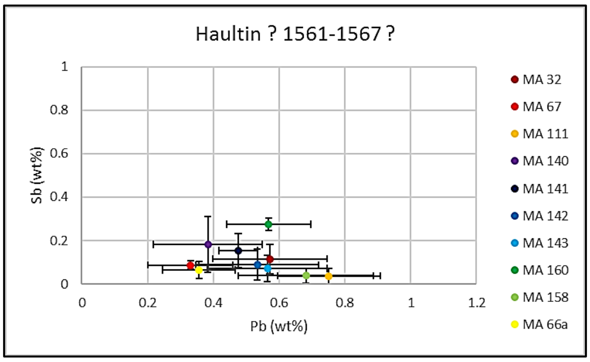

Fig. 5.44: XRF results on matrices possibly by Haultin, Paris.

5.4.3.2.6 Pierre Haultin

The matrices MA 32, 66a, 67, 111, 140, 141, 142, 143, 158, 160 are likely to be attributed to Haultin in the period 1561-1567 (Fig. 5.44). The analytical results all show very low Sb concentrations (under 0.2 wt%, except for MA 160). The locations of Haultin in these years varies between Paris, Lyon and possible other places. Therefore, it is difficult to attribute the results to a certain city; however, the very low Sb levels resemble other measurements that can be linked to Paris (Le Bé) or Lyon (Granjon).

5.4.3.2.7 Silvius

The matrices MA 21, dating c. 1567 in Silvius' prints, are made in brass and explained in part 5.4.3.3 (Brass matrices). It appears to be one of a kind among the matrices measured in this project. Plantin used it from 1580 onwards, therefore it is plausible that he acquired the set from Silvius.

5.4.3.2.8 Tavernier

The set of matrices MA 163 could be attributed to Tavernier, dating c. 1561. Two kinds of copper are in this set, one major group with average Pb/Sb concentrations (0.4/0.4 wt% ±0.1) and one minor group, also containing arsenic (Pb 0.3 wt% ±0.1, Sb 0.4 wt% ±0.02 and As 0.6 wt% ±0.1). The compositions resemble measurements on matrices by Granjon (Antwerp period) and Hendrik van den Keere (Ghent), in any case apparently related to Flanders around 1560.

5.4.3.2.9 Bomberghens

Dated 1565, there are a few sets that point to the Bombergh family: MA 24, 135bc, 167a. The results for these 4 sets lie within each other's deviation values, making it possible that they come from the same source of copper. Also, the results from 135a show an extreme match with 135b and 135c (see Appendix). It is therefore suggested that they could all belong to the same strike-maker (Fig. 5.45).

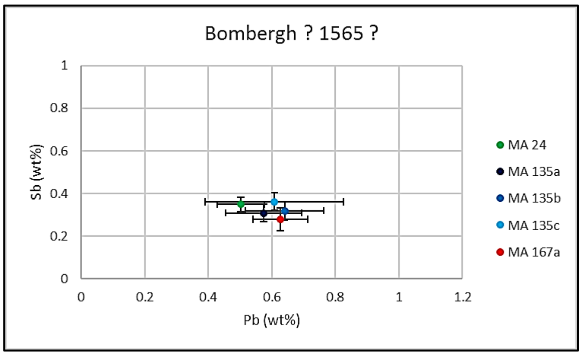

Fig. 5.45: XRF results on matrices possibly by the Bomberghens.

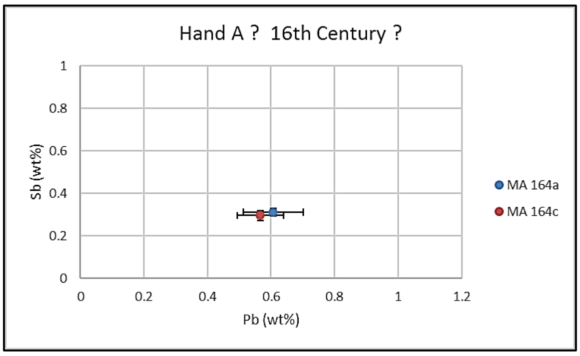

Fig. 5.46: XRF results on the unknown 'Hand A' matrices' compositions.

5.4.3.2.10 Hand A

This attribution is supposed to be an unknown cutter from the early or mid-16th century (Parker & Melis, 1960). Two of the faces are Hebrews connected to the Bomberghs. The analytical result on set MA 164c seems to support this idea. Moreover, not only MA 164c but also MA 164a are almost identical to each other, making it probable that they come from a similar copper source.

5.4.3.2.11 Franciscus Raphelengius

Raphelengius, active in the period 1590-1652, was connected to 4 (parts of) sets of matrices, namely MA 30, 73ab, 126 (Parker, Melis, & Vervliet, 1960). MA 73a and 73b do match each other in composition; MA 30 is close in its results (Fig. 5.47). For MA 126, the suggestion (Parker, Melis, & Vervliet, 1960) that Raphelengius may have had this strike made when he had the punches is unlikely, given the measurements. The quite unique alloy without any Sb and very low Pb points with the measurements done until now, exclusively to matrices as from Le Bé's hand.

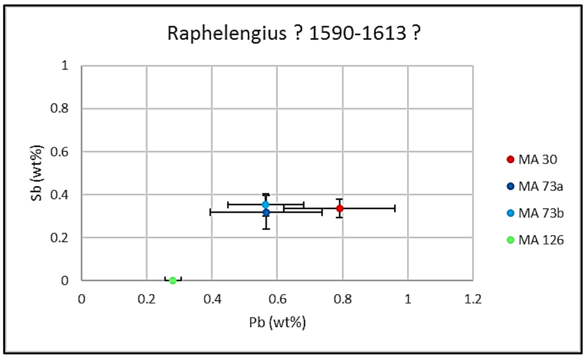

Fig. 5.47: XRF results on matrices, possibly by Raphelengius.

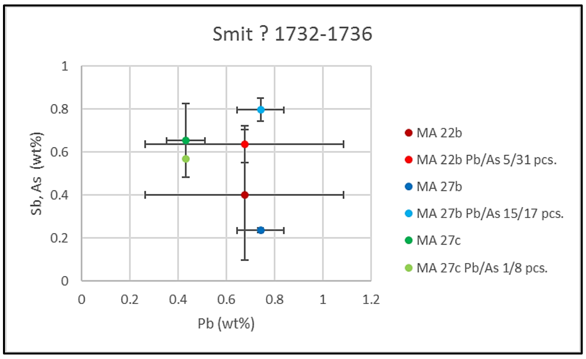

Fig. 5.48: XRF results on 18th century copper compositions, possibly by Smit.

5.4.3.2.12 Johan Michael Smit

The analytical results on matrices MA 22b and 27bc, dating 1732-1736 for Smit's work, show a mix of coppers with and without arsenic and overall a large variation in composition (Fig. 5.48). This complies with earlier measurements of 18th century strike-makers.

5.4.3.3 Brass matrices

The majority of matrices were struck in copper. The copper as described by Biringuccio, Moxon and Fournier, who were prime authors on the subject, had to be as pure and soft as possible. Nonetheless, in the collection of matrices at the Museum Plantin-Moretus, there are a number of sets and sometimes individual matrices that are made of brass*. A number of them were selected on the basis of difference in colour(Table 5.3).

Table 5.3: Matrices selected on their yellowish appearance as opposed to the reddish-brown copper matrices from the Museum Plantin-Moretus collection.

Matrices sets or parts of sets (denoted *)	**Punchcutter/Matrix-maker**	**Year**
MA 15	Granjon	1561
MA 51* 52* 147 172e*	Granjon ?	1560-1561
MA 58a*	Granjon ?	1561-1562
MA 27a	Guyot ?	1563-18th C
MA 21	(via) Silvius ?	1567
MA 10	Unknown	18th C ?

The results (Fig. 5.49,) show that the majority of the Pb-Sb concentrations of the brass matrices are respectively 0.8/0.1 wt%. Two results stand out: MA 10 and a part of MA 27a. The Zn-Sn concentrations show 4 distict groups (Fig. 5.50); central, an 8 wt% Zn and approx. 0.4 wt% Sn; left, a group with very little Zn, and two separate sets: MA 10 and MA 21 that do not relate to any of the others.

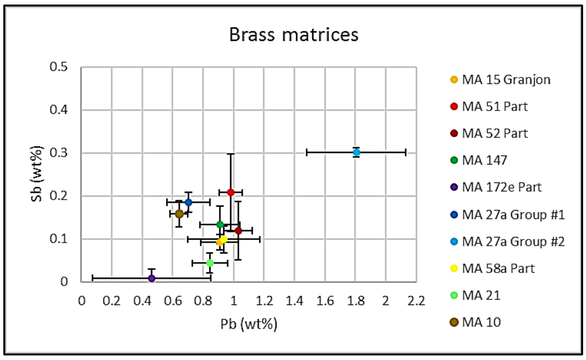

Fig. 5.49: XRF results for Pb-Sb concentrations of the selected brass matrices.

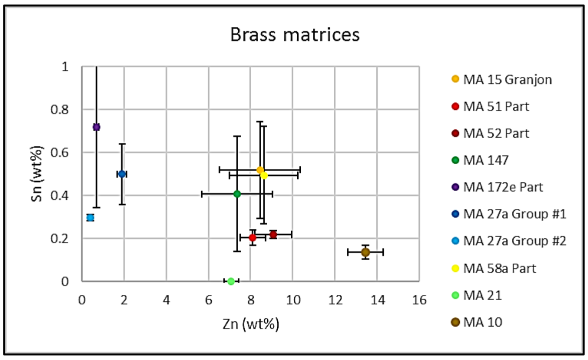

Fig. 5.50: The Zn-Sn concentrations of the brass matrices, as in Fig. 5.49.

The matrices by Granjon (MA 15), and the matrices probably attributed to Granjon (Part of MA 58a and MA 147) are a very close group in their Pb/Sb and Zn/Sn contents. The results for MA 51 and MA 52 have slightly larger deviations in the Sb concentrations and smaller deviations in the Zn/Sn concentrations. This does not exclude that these matrices are from Granjon's hand, but if so, it is considered that they were not produced from the same batch of brass as the former group.

MA 21 does not fit any of the other clusters with its very low Sb content and absence of Sn in the brass. This Fractur-letter possibly has a German origin.MA 10 also differs from the other sets with quite a high Zn-content, leaning between red and yellow brass in composition. The origin of this set is unknown, but is thought to be 18th century. These are matrices from large punches, proving that it was certainly possible to strike brass matrices.

The matrices MA 27a and 172e are partially made of 'brass'. However, the Zn content is so low (between 0.4 and 1.9 wt%) that this alloy should be called copper with Zn and Sn impurities in addition to the Pb and Sb contents. They do not correspond to the sets of matrices attributed to Granjon.

5.4.3.4 Arsenic copper matrices

Besides the brass matrices, there is another group of alloys that might be interesting to look at, namely the coppers with arsenic content. Arsenic as a trace metal in the copper was measured in 16th and 18th centuries coppers. As opposed to former graphs, where for the coppers mainly Pb and Sb were pairwise presented as analytical results, here the Sb-As ratio is shown (Fig. 5.51). A comparison of 16th century arsenic copper from Hendrik van den Keere and 18th century alloys from Smit, Van Wolsschaten and Rosart shows that the early copper has Sb/As levels of approx. 0.7/0.4 wt%. The different sets of matrices from Van den Keere are shown in detail in Fig. 5.52.

The 18th century alloys all have lower Sb concentrations (c. 0.2 wt%), whilst the arsenic concentration varies significantly. However, with respect to the latter it should be noted that quantifying As from the XRF spectrum is less reliable than for the other elements as discussed before. Nonetheless, a distinction between the two eras seems possible.

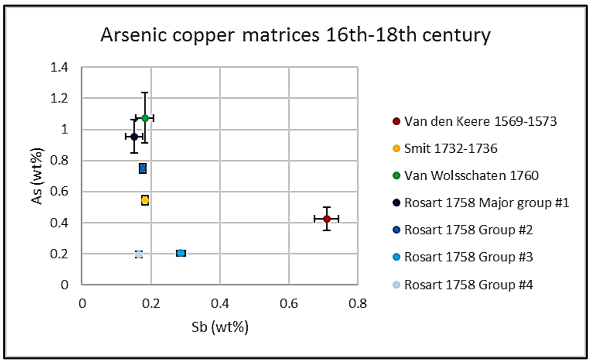

Fig. 5.51: XRF results for arsenic coppers, showing the Sb-As concentrations.

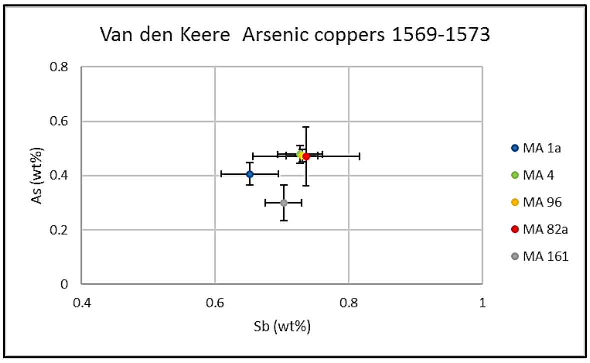

Fig. 5.52: Detail of the group arsenic coppers attributed to Van den Keere, from Fig. 5.51, Sb-As concentrations.

5.4.3.5 Other matrices

A last group of non-attributed matrices is defined in Table 5.4. The results of the analytical measurements are to be found in the Appendix. For the comparison to other sets and possible attributions, the statistical grouping method was used (5.4.3.6).

Table 5.4: List of non-attributed sets of matrices.

Punchcutter/ Matrix-maker	Matrices sets or matrix additions (denoted *)	Year
Unknown	MA 5a 5b 131a 167b	15th-16th C
Unknown	MA 27d 53a 66b 83b 83c 131b 135a 164a 171 172abcdfg 174 188jkps 146 79b 22a	16th C
Unknown	MA 77	16th / 18th C
Unknown	MA 58b	17th-18th C
Unknown	MA 10 47c	18th C
Unknown	MA 188abc	19th-20th C
Unknown	MA 28 56b 79a 117 188r	?

5.4.3.6 Statistical grouping

5.4.3.6.1 Method

Statistical grouping was performed as shown in the former part ‘Proof of principle’ (see 5.4.2.4). The selected matrices sets or parts of sets, each with a dedicated description in the Parker-Melis Inventory, are listed in the Appendix, together with their plotted XRF results. The numeric results from the XRF software were used to perform the statistical grouping. As in the former part, all 8 measured elements in the matrices, besides the copper, were taken into account (Pb, Sb, Zn, Sn, Ag, Fe, Ni, As).

The optimal number of clusters can be determined using previous knowledge on the data, but can also be estimated by determining the within-cluster dissimilarities for a varying number of clusters. An increasing number of clusters inevitably reduces the within-cluster dissimilarity decreases, but the relationship is not linear. The graph (Fig. 45) plotting within-cluster dissimilarity versus the number of clusters (referred to as the scree plot) typically shows a very sharp drop for a low number of clusters, followed by a bend and an almost horizontal line as the number of clusters increases. The optimal number of clusters is situated around the bend, but there are often many valid solutions.

In the current study, individual letters were grouped into clusters based upon the concentrations of the 8 metals measured in each letter. The Euclidean distance was used as a metric to calculate the dissimilarities. As a clustering technique, we used the Partitioning Around Mediods (PAM) algorithm, since it provides a clustering that is robust against outliers and extreme observations. To determine the optimal number of clusters, we applied PAM with the number of clusters ranging from 2 to 15. This showed that all solutions between 7 and 13 clusters would be acceptable.

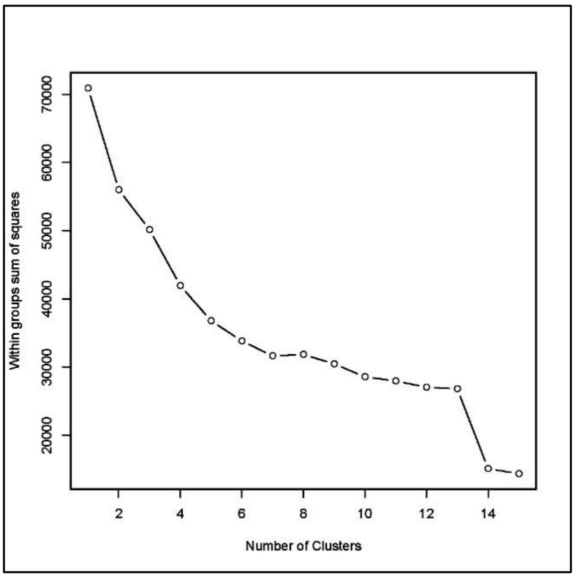

Fig. 5.53: Ratio Number of Clusters versus Results within groups sum of squares.

The optimum grouping was found to be in 10 clusters, based on the number of clusters/within groups sum of squares ratio graph and on the comparison with the results on MA 120 etc., as shown in the former chapter. Another choice from the graph could be 7 clusters, since the graph ratio levels at that point; however, it was found that there was too little distinction between the numerous sets, even with 9 clusters. Only from 10 clusters or more, was the one set of lead matrices (MA 9) shown as a separate group from all the other sets that consist of copper alloy matrices.

5.4.3.7 Clustering results for all measured sets and subsets

Each of the (sub-) sets of matrices was attributed by the statistical clustering to one or more clusters. Individual matrices' attributions can be found in the Appendix. Some of the sets have a majority of matrices attributed to one cluster and a few individual matrices attributed to other clusters (e.g. MA 1a). Other sets are consistent in the measurement results and are to be found within 1 cluster (e.g. MA 4). A last group of sets is dispersed in their copper composition results and is therefore attributed to a number of clusters (for example, MA 3).

Table 5.5: Results of the statistical grouping in 10 clusters (rows 1-10), showing the number of attribution of individual matrices in each set or subset. The first 10 sets of matrices are listed here.

Matrices	1	2	3	4	5	6	7	8	9	10
MA1a	23	1	1	1	1	0	0	0	0	0
MA1b	3	2	2	2	59	3	0	0	0	0
MA2	0	47	0	0	32	2	1	0	0	0
MA3	13	42	7	0	16	0	0	0	0	0
MA4	61	0	0	0	0	0	0	0	0	0
MA5a	0	0	0	21	0	0	0	0	0	0
MA5b	0	0	0	0	0	0	0	23	0	0
MA6	0	22	0	2	9	0	0	0	0	0
MA7	0	0	3	0	6	0	0	0	1	0
MA8	0	0	2	0	6	0	0	0	0	0
MA9	0	0	0	0	0	0	0	0	0	23
MA10	0	1	0	0	0	0	27	0	0	0
The rest of the list can be consulted in the Attachments.										

5.4.3.7.1 Cluster definitions

The algorithm used by the statistical programme has led to the formation of the above clusters. To define the alloy compositions of the matrices that were attributed to each of the clusters, the following averaged compositions with their standard deviation were calculated (Table 5.6). It can be noted that some of the clusters show high standard deviation values versus the average, meaning that the group of this element is quite broad (for example, Pb in Cluster 1: 0.37 wt%, ±0.28). Other groups are more confined (for example, Sb in Cluster 5: 0.43 wt%, ±0.09) or the deviation is larger than the average value (for example, As in Cluster 4: 0.01 wt%, ±0.06). This last fact is to be explained from the individual results, showing that there is a minority of matrices present with As concentrations in this cluster, but that they are averaged out by the majority of matrices not containing any As. In these cases the statistical algorithm gave preferences to other elements and their concentrations, over the As content.

Table 5.6: Averaged cluster compositions, alloy elements in wt% and standard deviation values (copper is the balance). Red numbers are the highest values, green the lowest in the column. Row 1 and 9 in pink include As contents; Row 7 are the brass alloys; Row 10 is the lead matrices set.

	Pb	Sb	Sn	Zn	Fe	Ag	Ni	As
1	0.37 *(±0.28)*	0.69 *(±0.14)*	0.00 *(±0.01)*	0.00 *(±0.02)*	0.04 *(±0.05)*	0.13 *(±0.05)*	0.07 *(±0.08)*	0.35 *(±0.21)*
2	0.57 *(±0.35)*	0.10 *(±0.08)*	0.02 *(±0.06)*	0.02 *(±0.19)*	0.04 *(±0.05)*	0.06 *(±0.01)*	0.09 *(±0.05)*	0.01 *(±0.04)*
3	0.39 *(±0.18)*	0.25 *(±0.06)*	0.00 *(±0.01)*	0.00 *(±0.00)*	0.02 *(±0.02)*	0.04 *(±0.01)*	0.09 *(±0.02)*	0.00 *(±0.03)*
4	0.73 *(±0.33)*	0.11 *(±0.11)*	0.01 *(±0.02)*	0.00 *(±0.03)*	0.04 *(±0.06)*	0.04 *(±0.02)*	0.34 *(±0.10)*	0.01 *(±0.06)*
5	0.53 *(±0.26)*	0.43 *(±0.09)*	0.00 *(±0.01)*	0.00 *(±0.02)*	0.03 *(±0.04)*	0.04 *(±0.01)*	0.08 *(±0.02)*	0.00 *(±0.00)*
6	0.39 *(±0.22)*	0.02 *(±0.05)*	0.01 *(±0.03)*	0.00 *(±0.00)*	0.03 *(±0.03)*	0.10 *(±0.01)*	0.01 *(±0.02)*	0.00 *(±0.00)*
7	0.88 *(±0.18)*	0.11 *(±0.06)*	0.37 *(±0.29)*	7.56 *(±3.08)*	0.23 *(±0.16)*	0.06 *(±0.02)*	0.25 *(±0.06)*	0.00 *(±0.00)*
8	0.59 *(±0.31)*	0.32 *(±0.12)*	0.00 *(±0.02)*	0.01 *(±0.07)*	0.07 *(±0.08)*	0.00 *(±0.01)*	0.08 *(±0.03)*	0.04 *(±0.14)*
9	0.38 *(±0.14)*	0.18 *(±0.04)*	0.03 *(±0.04)*	0.00 *(±0.02)*	0.03 *(±0.04)*	0.07 *(±0.02)*	0.09 *(±0.03)*	0.97 *(±0.16)*
10	96.43 *(±2.50)*	1.11 *(±2.03)*	1.96 *(±1.29)*	0.00 *(±0.01)*	0.16 *(±0.16)*	0.00 *(±0.00)*	0.00 *(±0.00)*	0.00 *(±0.00)*

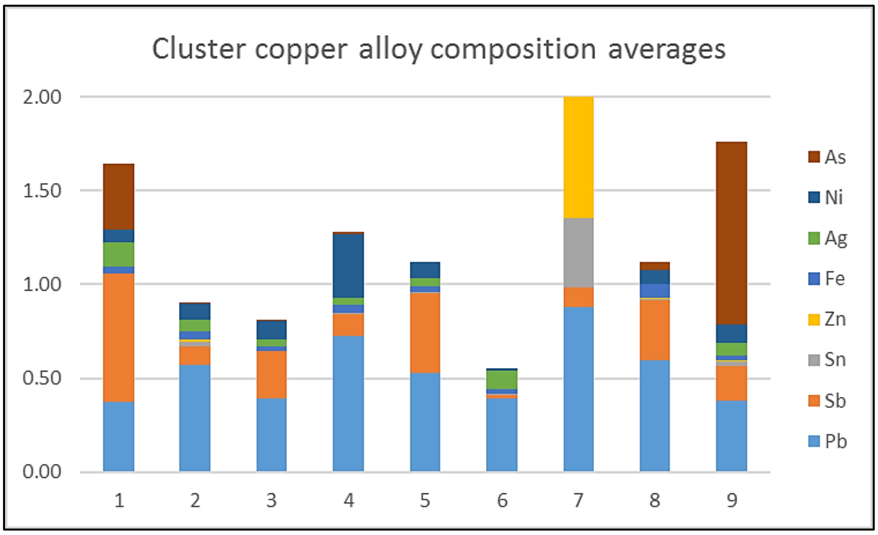

Fig. 5.54: Graphic presentation of the average composition for each cluster, as described in detail in Table 5.6.

Notes on Fig. 5.54: Cluster 10, consisting of lead matrices only, is not in this graph because the Pb/Sn ratios are too high to fit within the graph. Cluster 7 represents brass matrices whereas the zinc content is actually 7.56 wt%, but limited here to 2 wt% for the readability of the graph; therefore the small amounts of iron, silver and nickel are not visible for this cluster (see Table 5.6).

5.4.3.7.2 Matrices relations within clusters

Matrices within a cluster, based on their compositional similarities, are evaluated on other possible mutual factors such as strike-maker, period or location. To do this, all (sub-) sets of matrices were normalised to 100 for comparison purposes. Because some (sub-)sets consist of over 150 individual matrices and some as little as 3, it was important to acquire a view on the homogeneity of each measured set. Table 5.5 shows that many sets consist of different kinds of copper (for example, MA 3), while others are very homogeneous (for example, MA 4), and shows only 1 group of copper that was used to make the set. For the purpose of finding correlations between matrices compositions, attributed makers and their period and location, only the (sub-) sets with over 50% of matrices within a certain cluster were considered.

The following list (Table 5.7) gives per cluster the three different groups: firstly, the archival documented attribution of matrices; secondly, the probable attributions of matrices (followed by a question mark); and finally, the matrices that have no attribution (showing only question marks). As explained above, the right column is the percentage of matrices in the particular set, belonging to the cluster described.

Table 5.7: Grouping of strike-makers, their period, location and specific matrices (sub-) sets, in which at least 50% of the matrices was attributed to each of the clusters.

Strike-maker	**Period**	**Location**	**Matrices**	**Cluster 1**
Hendrik van den Keere	1570	Ghent	MA4	100%
Hendrik van den Keere	1570	Ghent	MA1a	85%
Hendrik van den Keere	1572	Ghent	MA82a	64%
Strike-maker	**Period**	**Location**	**Matrices**	**Cluster 2**
Guillaume Le Bé I	1566-1568	Paris	MA40	95%
Guillaume Le Bé I	1551-1562	Paris	MA72	67%
Guillaume Le Bé I	1559-1563	Paris	MA6	67%
Guillaume Le Bé I	1573	Paris	MA47a	53%
Guillaume Le Bé I ? Garamond ?	1563 ?	Paris ?	MA2	57%
Le Bé I ? (H. van den Keere ?)	1561? (1570 ?)	Paris ? (Ghent ?)	MA3a (3b)	54%
Haultin ? Le Bé ?	1557 ?	Paris ? Lyon ?	MA66a	65%
Pierre Haultin ?	1561 ?	Paris ? Lyon ?	MA32	90%
Pierre Haultin ?	1561? 1567 ?	Paris ? Lyon ?	MA143	79%
Pierre Haultin ?	1561? 1567 ?	Paris ? Lyon ?	MA142	78%
Pierre Haultin ?	1561 ?	Paris ? Lyon ?	MA67	68%
Pierre Haultin ?	1561 ?	Paris ? Lyon ?	MA141	60%
Claude Garamond ?	1563	Paris ?	MA59	96%

Robert Granjon	1567-1569	Antwerp	MA128	66%
Robert Granjon ?	1566 ?	Antwerp ?	MA47b	65%
Robert Granjon ?	1561 ?	Lyon ?	MA52	56%
Granjon ? Guyot ? Smit ?	1563? 18thC?	Lyon ? Antwerp ?	MA27a	54%
Granjon ? Guyot ?	1561? 1562 ?	Lyon ? Antwerp ?	MA58a	51%
Claude Garamond ?	1563	Paris ?	MA60	61%
Unknown	?	?	MA117	94%
Unknown	15th-16th C ?	?	MA167b	60%
Unknown	16th C ?	?	MA172g	56%
Strike-maker	**Period**	**Location**	**Matrices**	**Cluster 3**
Robert Granjon	1574	Paris	MA134	95%
Robert Granjon	1574	Paris	MA184	91%
Robert Granjon	1574	Paris	MA191	88%
Robert Granjon	1574	Paris	MA156	87%
Robert Granjon	1574	Paris	MA120	86%
Robert Granjon ?	1576 ?	Lyon ?	MA54b	89%
Pierre Haultin ?	1565 ?	Paris ?	MA160	54%
Hendrik van den Keere	1575	Ghent	MA70	75%
Hendrik van den Keere	1574	Ghent	MA93	75%
Hendrik van den Keere	1572	Ghent	MA92e	67%
Hendrik van den Keere	1576	Ghent	MA62	60%
Hendrik van den Keere	1577	Ghent	MA91a	52%
Hendrik van den Keere	1578	Ghent	MA102	50%
Hendrik van den Keere ?	1573 ?	Ghent ?	MA148	66%
Hendrik van den Keere ?	?	Ghent ?	MA145	64%
Hendrik van den Keere ?	?	Ghent ?	MA144	58%
François Guyot ?	?	Antwerp ?	MA153	75%
Via Bombergh ?	1565 ?	?	MA167a	69%
Franc. Raphelengius ? Hand B ?	1591-1597 ?	Leiden ?	MA73a	52%
Unknown	16th C ?	?	MA66b	100%
Unknown	16th C ?	?	MA172b	91%
Unknown	1555 ?	?	MA146	87%
Unknown	16th C ?	?	MA83b	68%
Unknown	16th C ?	?	MA135a	62%
Unknown	16th C ?	?	MA164a	60%
Hand A ?	16th C ?	?	MA164c	60%
Unknown	1550? 18th C?	?	MA77	53%

Strike-maker	**Period**	**Location**	**Matrices**	**Cluster 4**
Unknown ? Robert Granjon ?	1561 ?	? Lyon ?	MA22a	94%
Robert Granjon ?	1561 ?	Lyon ?	MA23	90%
Robert Granjon ?	1579 ?	Rome ?	MA49b	77%
Robert Granjon ? Guyot ?	1566 ? 1567 ?	Antwerp ?	MA36b	73%
Granjon ? Guyot ? Le Bé ?	1563? 1565 ?	Antwerp ? Paris ?	MA53b	68%
Haultin ? Hamon ?	1561 ?	Paris ? Lyon ?	MA158	100%
Pierre Haultin ?	1561 ?	Paris ? Lyon ?	MA111	80%
Pierre Haultin ?	1561 ?	Paris ? Lyon ?	MA140	76%
Le Bé I ? Garamond ?	1561? 1571 ?	Paris ?	MA20b	80%
Le Bé I ? Garamond ?	1561? 1571 ?	Paris ?	MA20a	50%
Unknown	15th-16th C ?	?	MA5a	100%
Unknown	16th C ?	?	MA172f	60%
Unknown	18th C ?	?	MA47c	55%
Strike-maker	**Period**	**Location**	**Matrices**	**Cluster 5**
Robert Granjon	1570	Antwerp	MA182	98%
Robert Granjon	1570	Antwerp	MA119	95%
Robert Granjon	1571	Antwerp	MA122	95%
Robert Granjon	1570	Antwerp	MA183	95%
Robert Granjon	1570	Antwerp	MA118	92%
Robert Granjon	1570	Antwerp	MA121	88%
Robert Granjon	1570	Antwerp	MA11	88%
Robert Granjon ?	1572 ?	Paris ?	MA63	97%
Robert Granjon ?	1560 ?	Lyon ?	MA110	83%
Robert Granjon ?	1569 ?	Antwerp ?	MA8	75%
Robert Granjon ?	1573 ?	Paris ?	MA71	68%
Robert Granjon ?	1566 ?	Antwerp ?	MA26a	66%
Robert Granjon ?	1569 ?	Antwerp ?	MA7	60%
Granjon ? Guyot ?	1566? 1567 ?	Antwerp ?	MA101c	96%
François Guyot ?	1555 ?	Antwerp ?	MA69	93%
François Guyot ?	1562	Antwerp ?	MA36a	85%
François Guyot ?	16th C ?	Antwerp ?	MA131b	70%
François Guyot ?	1557 ?	Antwerp ?	MA31	61%
François Guyot	1562	Antwerp ?	MA57	85%
Hendrik van den Keere	1573	Ghent	MA91b	86%
Hendrik van den Keere	1573	Ghent	MA1b	83%
Hendrik van den Keere	1569	Ghent	MA68	69%
Hendrik van den Keere	1571	Ghent	MA92d	67%
Hendrik van den Keere	1570	Ghent	MA96	58%
Tavernier ?	1561 ?	Antwerp ?	MA163	80%
François Guyot / Bombergh ?	1564	Antwerp?	MA34	69%
Franc. Raphelengius ? Hand B ?	1591-1597 ?	Leiden ?	MA73b	86%

Johan Michael Smit ?	1732-1736 ?	Antwerp ?	MA27c	88%
Smit ?	1560 ? 18th ?	? Antwerp ?	MA79b	69%
Unknown	16th C ?	?	MA172d	100%
Unknown	16th C ?	?	MA27d	100%
Unknown	?	?	MA79a	96%
Unknown	16th C ?	?	MA53a	94%
Unknown	?	?	MA28	87%
Unknown	16th C ?	?	MA171	75%
Unknown	16th C ?	?	MA83c	65%
Unknown	16th C ?	?	MA172c	63%
Unknown	16th C ?	?	MA172a	60%
Strike-maker	**Period**	**Location**	**Matrices**	**Cluster 6**
Granjon ? Le Bé ? Raph. ?	1565 ? 17th C ?	Paris ? Leiden ?	MA126	97%
Hendrik van den Keere ?	1575 ?	Ghent ?	MA76	88%
Guyot ? Le Bé I ? Le Bé II ?	1561-1598 ?	Antwerp ? Paris ?	MA56a	64%
Unknown	?	?	MA83d	100%
Unknown	15th-16th C ?	?	MA131a	60%
Strike-maker	**Period**	**Location**	**Matrices**	**Cluster 7**
Robert Granjon	1561 ?	Lyon	MA15	94%
Robert Granjon ?	1561 ?	Lyon ?	MA147	100%
Via Silvius ?	1567 ?	Germany ?	MA21	95%
Unknown	18th C ?	?	MA10	96%
Strike-maker	**Period**	**Location**	**Matrices**	**Cluster 8**
V d Keere ? Raph. ?	1572 ? 1590-1613 ?	Ghent ? Leiden ?	MA30	70%
Via Bombergh ?	1566 ?	?	MA135c	52%
Claude Garamond ?	1561 ?	Paris ?	MA25a	56%
Unknown	15th-16th C ?	?	MA5b	100%
Strike-maker	**Period**	**Location**	**Matrices**	**Cluster 9**
Jacques François Rosart	1758	Haarlem	MA151	100%
Jacques François Rosart	1758	Haarlem	MA45	100%
Jacques François Rosart	1758	Haarlem	MA46	69%
Jean-Baptiste Van Wolsschaten	1760	Antwerp	MA35	99%
Johan Michael Smit ?	1732-1736 ?	Antwerp ?	MA27b	88%
Unknown	16th C ?	?	MA174	100%
Unknown	17th-18th C ?	?	MA58B	100%
Strike-maker	**Period**	**Location**	**Matrices**	**Cluster 10**
Sabon ?	1561-1570 ?	Antwerp ?	MA9	100%

5.4.3.7.3 Compilation of the results per cluster

Gathering the findings from the above list (Table 5.7), comments for each cluster are given below. As a reminder, the average composition of the alloys in each cluster is given in the heading of the paragraph (concentrations of the elements which are present, equal to or exceeding 0.1 wt%, in wt%).

Cluster 1 (Pb 0.4, Sb 0.7, Ag 0.1, As 0.4)

This cluster with copper composition including lead, antimony, (some silver) and arsenic, consists of 3 attributions to Hendrik van den Keere between 1570 and 1572: MA 1a, MA 4 and MA 82a. He lived and worked in Ghent. For the 16th century, these are the only sets of matrices which also contain As together with parts of MA 96 and MA 161, which are also attributed to Van den Keere, respectively from the years 1570 and 1573. No non-attributed sets fall within this cluster.

Cluster 2 (Pb 0.6, Sb 0.1)

Cluster 2 is significant for its very low antimony contents and overall purity compared to other clusters. In this group, the most important contributor is Guillaume Le Bé I from Paris later than 1551 and before 1573 with the matrices MA 6, MA 40, MA 47a and MA 72. Matrices MA 2, MA 3 and MA 66a are also attributed to this group and could find their origin with Le Bé. Pierre Haultin also comes into the picture in this group with the sets MA 32, MA 67, MA 141 and MA 142-143. In addition, Haultin lived and worked in Paris, perhaps in Lyon, between 1557 and 1567. Claude Garamond and Robert Granjon also come into the picture with matrices in this group: MA 59, 60 for Garamond, MA 128, MA 47b and MA 52 for Granjon. The 3 non-attributed sets are uncertain within this cluster because of the small number of measurements (MA 172g and MA 167b) or because the average values for the Pb-content differs too much (MA 117).

Cluster 3 (Pb 0.4, Sb 0.3)

This cluster includes copper, which is relatively pure with only low quantities of Pb and Sb, similar to each other. Robert Granjon has 5 attributions in this set, namely the series of strikes MA 120 etc., also shown in the former part ‘Proof of principle’. At that time, 1574, Granjon lived in Paris. Another set before 1576, probably from Granjon, is in this group: MA 54b. The second main purveyor of matrices in this set is Hendrik van den Keere with 6 sets and 3 probable attributions, respectively MA 62, 70, 91a, 92e, 93, 102 and MA 144-145, 148. These were made in the periods 1570-1578 in Ghent. Besides 3 matrices sets, possibly from Guyot, Bombergh or Raphelengius, there are 8 non-attributed sets, which might lead towards Granjon or Van den Keere, based on the above results: MA 66b, 77, 83b, 135a, 146, 164a, 164c or 172b.

Cluster 4 (Pb 0.7, Sb 0.1, Ni 0.3)

Cluster 4 does not show any matrices attributed on archival grounds. There are probable attributions to Granjon in his Lyon period (MA 22a and 23, 1561) and Pierre Haultin in Paris or Lyon (MA 111, 140, 158, also 1561). Other names in this group are Le Bé and possibly Garamond, both living and working in Paris (MA 20a and b). MA 5a is also placed in this cluster but has much higher Pb values, leading to the conclusion that it probably has no link with the other names in this group.

Cluster 5 (Pb 0.5, Sb 0.4)

This cluster presents the series of strikes by Granjon MA118, etc., while he worked in Antwerp, 1570. MA 11 is also included in this group, with a series of other matrices attributed to Granjon between 1560 and 1573: MA 7, 8, 26a, 63, 71 and 110. MA 71 is especially noteworthy, as it was discussed in the previous part of this research. Another group that is attributed on archival grounds are 5 sets of Van den Keere: MA 1b, 68, 91b, 92d, 96 and the additions in MA 160. From Guyot, working in Antwerp with matrices between 1555 and 1562 are MA 57 (archival documented), MA 31, 36a, 69 and 131b (probable). Quite a large number of non-attributed sets fall within this cluster: MA 27d, 28, 53a, 79a, 83c, 171, 172a c and d.

Cluster 6 (Pb 0.4, Ag 0.1)

Cluster 6 is not attributed many times to particular sets of matrices: MA 76 is thought to be by Van den Keere (1575 ?), MA 126 and MA 56a are also uncertain. Two completely non-attributed sets are also in this group: MA 83d and MA 131a. Not much information can be derived from this cluster.

Cluster 7 (Pb 0.9, Sb 0.1, Sn 0.4, Zn 7.6, Fe 0.2, Ni 0.3)

This group is special because it contains the brass matrices. The sets that are placed in this group by the statistical method are MA 15 (Granjon, Lyon, around 1561) and a set that is probably from his hand and from the same period too: MA 147. Minor parts in other sets that can also be attributed to Granjon in his Lyon period can be found in other sets: MA 27a, 51-52, 58a (see 5.4.2.3), 172e. Other sets like MA 21 and MA 10 also contain zinc, but are not regarded as being from a same source. More details are in 5.4.3.3.

Cluster 8 (Pb 0.6, Sb 0.3)

Cluster 8 scarcely groups important sets. Only sets MA 5b (non-attributed), MA 25a (Garamond ?), MA 30 (Van den Keere, Raphelengius ?) and MA 135c (Bombergh ?) are found here. On the other hand, many minor parts (less than 50 % matrices in each set) are within this group. It is not easy to draw any conclusions from the results in this cluster.

Cluster 9 (Pb 0.4, Sb 0.2, As 1.0)

In addition to cluster 1, this is the only other cluster where the copper contains As and in even higher concentrations. The group contains 3 matrices sets by Rosart: MA 45-46 and MA 151, in addition to 1 by Van Wolsschaten (MA 35). Probably MA 27b by Smit also fits well in this cluster, making it exclusively 18th century and from the Low Countries. Two other non-attributed sets can also be found in this group: MA 174 (uncertain to be from the 16th century) and MA 58b (considered to be a later addition, see 5.4.2.3).

Cluster 10 (Pb 96.4, Sb 1.1, Sn 2.0, Fe 0.2)

The final cluster consists only of MA 9, which is a lead matrices set probably made by Sabon in Antwerp.

5.4.3.8 Discussion on the statistical grouping

The mathematical clustering has revealed a distinction of groups, the most prominent factors of which are summarised in the following table (Table 5.8): from the 145 selected (sub-) sets of matrices, 73 are more than 50 % homogeneous in their alloy composition, leading to an attribution in a particular cluster. Two of the clusters (6, 8) do not provide unambiguous results. Cluster 10 stands out because it contains the only set of lead matrices, as opposed to all the other copper alloy sets. Cluster 9 is dedicated to 18th century matrices while cluster 7 contains only the brass matrices. The first 5 sets are divided into alloy groups that were mainly used in the Low Countries (1, 5) or from France (2, 4). Cluster 3 seems to be a mix of locations, although it is not impossible that Granjon continued to use copper from the Low Countries after leaving Antwerp in 1570.

Statistical grouping is a tool for fast viewing of possible correlations. It is not strict in its outcomes and the results must be critically evaluated. For this purpose, each case should be studied in more detail. As an example, in some cases such as clusters 6 and 8, a minority of poor attributions was obtained and the sets of matrices in these groups seemed more rejected from other groups instead of dedicated to these clusters. However, the majority of results from the statistical grouping do largely resemble the results of the elemental comparison on the sets of matrices as in 5.4.2 and 5.4.3. With the obtained results, the two methods are considered complementary to each other. It also shows that both methodologies should be weighed against each other before drawing conclusions.

Table 5.8: Overview of the most prominent facts from mathematical clustering of the alloy compositions of matrices. The number of matrices sets (#) represent the matrices with at least 50 % of matrices within the cluster, for attributed and probable attributed sets to a strike-maker.

Cluster	Strike-maker	Period	Location	# matrices sets
1	Hendrik van den Keere	1570-1572	Ghent	3
2	Guillaume Le Bé I Pierre Haultin ? Robert Granjon	1551-1573 1557-1567 1561-1569	Paris Paris ? Lyon ? Antwerp / Lyon ?	6 5 3
3	Hendrik van den Keere Robert Granjon	1570-1578 1574-1576 ?	Ghent Paris / Lyon ?	10 6
4	Granjon ? Haultin ? Le Bé ? Garamond ?	1561-1571 ?	Paris / Lyon ?	10
5	Robert Granjon Robert Granjon ? François Guyot Hendrik van den Keere	1570-1571 1560-1573 ? 1555-1562 ? 1569-1573	Antwerp Lyon-Antwerp-Paris ? Antwerp ? Ghent	7 6 5 5
6	Not consistent results			
7	Robert Granjon	1561	Lyon	2
8	Not consistent results			
9	Jacques François Rosart Jean-Baptiste Van Wolsschaten	1758 1760	Haarlem Antwerp	3 1
10	Sabon ?	1561-1570 ?	Antwerp ?	1

5.4.4 Discussion on all results

The results from the measurements and their correlations can be considered on three levels. First of all, the alloy composition differences of individual matrices within a set can be significant for comparison in the set or exclusion from the (original) set. Secondly, average alloy compositions of a majority of matrices within a set can be related to other sets of the same strike-maker, location and period in a number of cases. A particular observation is the more widespread use of brass matrices. Thirdly, the results offer a view on the use of what was considered to be pure copper in the researched periods, i.e. in this study mostly the second half of the 16th century and the mid-18th century.

5.4.4.1 Alloy composition differences within a set of matrices

The XRF analytical technique used for measuring and quantifying metals in the copper and alloys of the matrices has shown that it is applicable for distinguishing matrices from each other, disregarding any visual aspect. Former studies have been made on grounds of the faces that were struck with the punches, but also on what the strikes looked like or how the matrices were finished, hence tool traces, shapes and sizes of the matrices. In most of the cases, it appears that previously drawn conclusions can be supported by the analytical measurements.

The XRF technique entails a surface analysis that is beneficial because no sampling is needed; however, it does have its limitations because it is not possible to analyse the true bulk material. Nonetheless, oxidation layers have proved not to be hugely influential when quantifying the elements present in the alloy. As an example, MA 182 has pink (copper) coloured and black strikes throughout the set (Fig. 5.55 and Fig. 5.56), yet the lead-antimony values in the copper gave similar results (Fig. 5.57).


Fig. 5.55: Set MA 182

Fig. 5.56: Detail

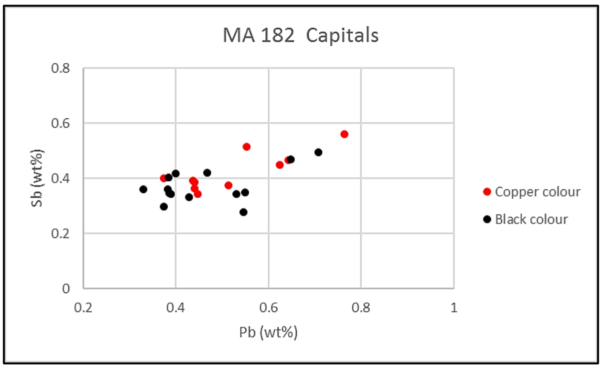

Fig. 5.57: Results of blank and black coloured strikes random throughout the measurements.

Small or large matrices do sometimes seem to come from different sources of copper, which is not surprising since the coppersmith had to produce rods of copper to the dimensions that the punchcutter had given, in the form of wooden models. As an example, the set of matrices MA 6 from Le Bé, his famous ‘Gros Hebreu Fort Gros’, N°10 is chosen to illustrate this (Fig. 5.58). The majority of the matrices are impressively large, and come from even larger strikes. Since the punches are also large and much force had to be used to strike them, the copper had to be as soft as possible. Le Bé was able to choose the purest copper he could find, without any antimony and only small traces of lead. For the smaller glyphs, another kind of copper was used and apparently posed no problem because these matrices have been shown to contain higher amounts of lead as well as antimony (Fig. 5.59).

Fig. 5.58: Hebrew matrices MA 6 from Le Bé, about 1560.

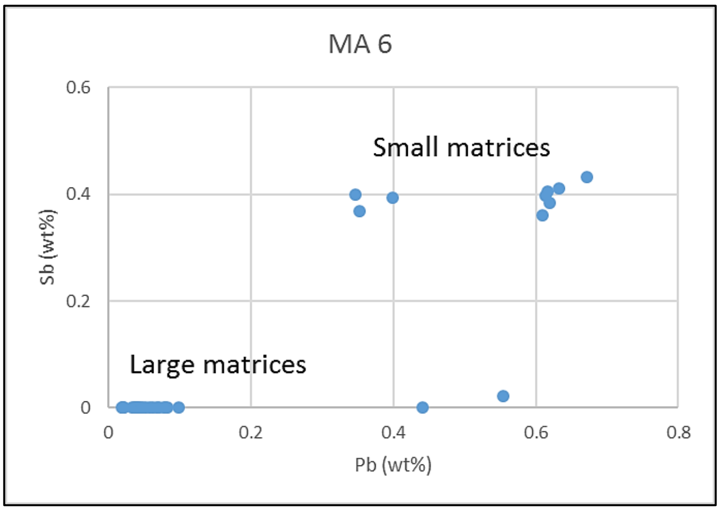

Fig. 5.59: Copper compositions (Pb/Sb content) of MA 6 in relation to the kind of matrices in the set.

Switches of matrices between sets or later additions to a set can be discovered using the techniques presented here, especially when the base set consists of homogeneous copper or brass. As an example, MA 24 that belonged to the Bomberghens is shown here (Fig. 5.60). From archival documents it is known that Granjon added 4 matrices in 1565 (Parker, Melis, & Vervliet, 1960). They are isolated with their composition from the other matrices in the set (red circle in Fig. 5.61). The green marks on 10 matrices is explained on the handwritten note: '*de 10 matrijzen met groen gestreept passen met de stempels van ST 56*' ('the 10 matrices with green marks fit with the punches of ST 56'). On the basis of composition, they cannot be distinguished from the other matrices in the set, except for the 4 additions that Granjon made. Besides these conclusions, 2 other matrices containing arsenic (bottom row, 16th from the left and 3rd last) are measured too (Fig. 5.61, yellow dots) and one matrix was made of extremely pure copper (2nd last in the set).

Fig. 5.60: MA 24, including a note and green pen markings on individual matrices.

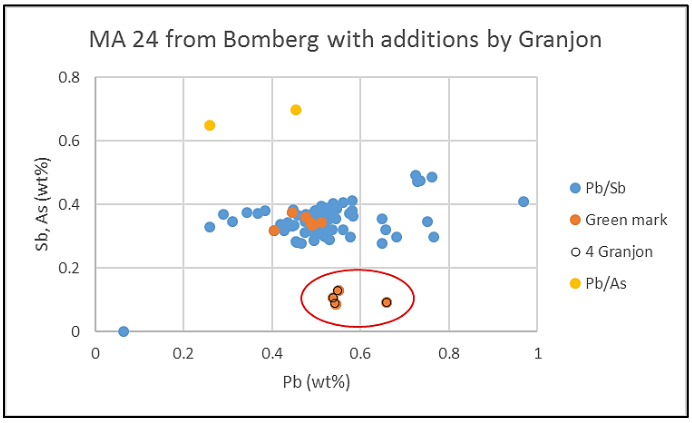

Fig. 5.61: The analytical results showing the 4 documented additions by Granjon (red circle).

5.4.4.2 Alloy compositions between sets of matrices

The analytical results show a number of similar compositions with sets that were definitely produced by the same punchcutter at the same time. The most prominent example is Granjon with his series MA 11, MA 118, etc., from 1570 and his series MA 120 etc., from 1574. Also the use of brass by Granjon is unique within the sets measured in this project.

In his earlier years of production Van den Keere seems to have used arsenic-containing coppers, something that has not been established for any other punchcutter from the 16th century until now. There is also a noticeable tendency for the copper that Van den Keere used to become more pure (lower Pb and Sb levels) towards the end of his career (1580). Others that worked in Flanders in the same period, like Guyot and Granjon when he was in Antwerp and De Vechter, as the successor of Van den Keere in Ghent, all seem to have used a similar kind of copper with medium concentrations of Pb and Sb.

In contrast, in Lyon Granjon had copper available with very low antimony concentrations and Le Bé in Paris even managed to get his hands on completely antimony-free copper that must have been of the highest quality on the market in the second half of the 16th century.

On the basis of these findings, again solely within the results of this project, certain conclusions can be drawn, albeit with caution. It is obvious that any possible conclusion about a certain attribution of matrices to one or another person, location or period should be supported by other complementary facts.

5.4.4.3 Copper in the 16th and 18th centuries

From the measurements it is clear that a wide range of coppers was used in the 16th century. The ‘pure’ copper that was available in this period always seemed to contain a minor percentage of lead. In most cases antimony was also found together with the lead, except with Le Bé who managed to obtain the purest copper without antimony and almost without lead.

In some cases, arsenic was also part of the copper, as measured in matrices by Hendrik van den Keere in his early period. And finally, not only copper but also (red) brasses were used as matrices. The majority of brass matrices in the MPM can be attributed to Granjon from his early Lyon period.

In the 18th century it appears that strike-makers used whatever kind of copper they could get their hands on. It seems contradictory that in later eras the copper was not more purified or homogeneous in quality. One could also conclude that the quality of the steel for the punches had improved because of the introduction of new production techniques (Tylecote, 1992). Because of the higher strength, hardness and toughness, it could be assumed that it became less important to choose the softest kind of copper because the newer steel could punch into any kind of copper alloy without breaking.

5.5 Conclusions

5.5.1 Phase 1

The results from the measurements in the initial project can act as a benchmark for further measurements on the MPM matrices collection. It was known from archival evidence and it has been confirmed here by the homogeneity of the results that the matrices MA 120, 134, 156, 184 and 191 were purchased by Plantin in a total order of 11 sets of strikes with the accompanying punches from Granjon in October 1574. The cursive capitals in the MA 71 set may also be by Granjon, whilst the other matrices in this set show divergent results. Even though there are strong similarities and arguments suggesting that the cursive capital matrices for MA 71 were harvested from MA 156, the findings give no exclusive answers.

As a case study, MA 76 was measured upon the assumption that the small capitals were moved from MA 71 to MA 76. Analysis has shown that this is very unlikely since no match in composition with MA 71 was found and the capitals do match with the other matrices in set MA 76, proving that this set is an integrated whole.

As a second case study, MA 58 was measured for its yellowish appearance. It proved to consist of a mix of copper and brass matrices, all struck with steel punches.

The results gathered in this research offer insights into the kind of copper the punchcutter/matrix-maker used. Despite the fact that they used ‘pure’ copper, the lead and antimony concentrations varied for each batch of copper they acquired. These results will not help to date the copper, although multiple measurements on the MPM collection could provide more specifications on the kinds of copper used by certain punchcutters/matrix-makers at a certain location and at a certain point in time. The next part, with extended measurements on large series of matrices, could provide more insight.

5.5.2 Phase 2

As a follow-up research of the ‘initial project’, the more profound investigation of matrices has shown to provide additional information. Together with the detailed results from the Appendix chapter, a number of relations between matrices’ alloy compositions, makers, location and period became visible. However, extended research should be carried out for an even larger statistical certainty and for more substantial evidence stating these first steps in connecting analytical with historical facts.

Strike-makers (mostly the punchcutters themselves in the 16th century) seem to have used large batches of copper to produce their strikes, since in many cases similar copper compositions are found throughout a number of matrices, attributed to a certain person. In the Low Countries, copper with moderate concentrations of lead and antimony were used, as were some coppers containing arsenic. In France, however, more pure copper with very low concentrations of antimony seemed to be commonly available. In strikes and matrices from the 18th century, again arsenic is found in the copper compositions, albeit with lower antimony concentrations and a higher homogeneity of the elements in the copper matrices.

An important find was the use of brass matrices, contradicting earlier assumptions that brass and bronze were only used to produce large casted matrices. Granjon, working in his early period in Lyon, seems to have used brass quite often. It is known that punchcutters and bookprinters were located very closely together on the banks of the Saone, together with the goldsmiths (Audin, 1954). It may not be a coincidence that the production and use of brasses led to the use of these alloys for the production of strikes. Another point of interest could be that Sabon also lived and worked in Lyon, and acquired a unique position in Frankfurt in 1575 to produce type with copper-based alloys. This could indicate that the use of brass was fairly common and well-known in Lyon and that Sabon mastered this knowledge to use in further experiments with the alloys for the production of not only matrices, but also type.

5.5.3 General conclusions

The XRF technique used could provide complementary proof for earlier research, raise some questions about former findings or bring new correlations to light on the origin and provenance of the matrices. It may also provide an insight into the use of copper throughout the 16th to 19th centuries and the evolution of refining techniques in combination with the sources and trade of the used copper.

Alloy composition differences

Homogeneity and differentiation is measurable within each set. In most cases, additions stand out concerning their copper composition. Earlier differentiation on a visual or documented basis often proves to correspond with the analytical results, but seems incorrect in some other cases. In some sets, a variation in copper composition is linked to the width of the individual matrices, showing that a different batch of copper was used for making wider and more narrow bars to produce strikes. Later additions also seem to connect with deviating copper compositions.

Relationships of alloy compositions to sets of matrices

Relationships between sets are shown in the case of strikes that were purchased on the same date, such as the sets ‘MA 118, etc.’ and ‘MA 120 etc.’ Other compositional similarities are noted and have focused the attention on some assumptions made earlier. The switching and adding of matrices from one set to another can be visualised with the results obtained.

Differentiation between punchcutters/matrix-makers

Within the limits of this study, the most prominent tendencies or differences between the copper compositions used by certain punchcutters can be specified for Hendrik van den Keere, Granjon and Le Bé. Throughout his production years Van den Keere used copper with medium levels of lead and antimony, although towards the end of his life the copper became slightly more pure, with lower concentrations of lead and antimony. In his earlier years, he used sometimes copper that also contained arsenic and that is not found with anyone else from the 16th century.

Granjon, on the other hand, had the opportunity of using more pure copper in his early Lyon period, but also used brass. When he was in Antwerp, it seems that he used local copper as it resembles the copper quality we find with Van den Keere. In his later periods, when he had left Antwerp, the copper he used was again more pure.

Le Bé is the only one throughout the measurements that managed to get copper that was completely free of antimony and in some cases even with extremely low lead concentrations. Within the present results, this distinguishes his matrices from the others.

Attribution to location

Subsequent conclusions can be drawn on the location in which the punchcutter lived and worked. The tendencies that come to the foreground are that the copper in Lyon and Paris in the 2nd half of the 16th century is more purified compared to copper that was available in the Southern Netherlands. In the MPM collection the use of brass for making matrices is mainly to be attributed to Granjon in his early Lyon period. However, other brass matrices which are present in the collection lead us to assume that brass matrices must have been produced in other locations too.

Copper in the 16th and 18th centuries

The matrices offer a documented insight into the use of 'pure' copper from the 16th to the 18th century. Trends in the use of copper containing a range of lead, antimony and arsenic concentrations are present. The exact quantification of these elements from the XRF spectra, especially arsenic, but also the low concentrations of iron and silver, is something that only could be approved using other measuring techniques. However, the presence of mainly lead and antimony in the copper seems to offer possibilities for distinguishing matrices. Besides the 'pure' coppers, the use of brass is highlighted and shows relevant grouping in some cases, but for most it remains an open question where brass was used and why brass was not used more frequently. Copper in the 18th century seems to be much less purified or homogeneous than one would expect. Arsenic is found on a number of occasions, but also the levels of lead and antimony (however lower than in the 16th century) are still present and in very varying concentrations.

Condition of the matrices at the MPM

Surveying and photographing all the matrices present at the MPM, this study also offers a view on the current state of the collection of matrices. Photographs of the complete sets are taken in high definition, allowing the reader or researcher to view individual characters within each set, enabling direct comparisons. This collection of photographs also serves as a record of the contemporary conservation state. Despite the fact that the majority of the matrices are in a good and stable condition, there are a number of corrosion issues. It also has to be noted that not all corrosion is visible on the faces of the strikes or matrices; sometimes corrosion has developed on the sides or backs of the copper, touching lead block fillings or the naked wood of the matrices' box. It was however beyond the scope of this research to go into detail on this aspect. A separate study is recommended. Finally, the photographs taken have to be considered as working material for the purposes of this study. It would be beneficial to make a series of new high-definition photos with a standardised set-up and lighting for further research and public online access purposes.

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6 Corrosion of lead type alloys and conservation

Publications related to this chapter:

Storme P., Jacobs M. and Lieten E. ‘*Research on corrosion of lead printing letters from the Museum Plantin-Moretus, Antwerp*’, in: Procedia Chemistry 8 (2013) p. 307-316.

Ghiara G., Campodonico S., Piccardo P., Martini C., Storme P. and Carnasciali M.: *‘Micro Raman investigation on corrosion of Pb-based alloy replicas of letters from the museum Plantin-Moretus, Antwerp’*, in: Journal of Raman Spectroscopy (2014) p. 1-10.

Content

6.1 Introduction

In 2011, at the request of the Plantin-Moretus museum, a study was performed on a corrosion problem that had been detected on some of the lead types (Storme, Jacobs, & Lieten, 2013). A research programme was designed to discover the precise cause of the corrosion processes and to suggest possible actions to prevent further damage to the types. In this initial research, which was limited in time and was considered to be the initial step with a view to a future research project, several methods of collecting data were chosen.

The occurrence of severe corrosion on some of the lead type, stored in the historic wooden trays used at the time of the active printing house, had to be investigated. Unlike when they were in use, the type had been resting for decades in the trays, closed with a hardboard lid for protection against the environment, mixing-up, loss or theft. This had led to the corrosion of some of the type, as recently discovered by the museum staff. It became clear that the source of the corrosion had to be sought in the combination of environmental parameters on the one hand and the composition of the lead type alloys on the other.

Fig. 6.1: Four types from left to right: without corrosion; with an even dark grey corrosion; with a dense white layer of passive corrosion and finally an example of a vigorously corroded item that has lost all structural rigidity, form and readability.

Firstly, a selection was made from the wooden boxes (trays), containing the lead letters on which corrosion formation had been detected. Secondly, all available historical and environmental data was collected to detect possible correlations. Thirdly, extensive macroscopic and microscopic observations were performed on selected items from the collection. Fourthly, analytical instruments such as XRF, SEM-EDX and XRD were used to collect chemical data on the alloy compositions and the corrosion. The fifth part of the project involved surveying the ambient environment in the museum itself. For this, lead coupons and two representative Pb alloys (i.e. Pb 70 wt% with respectively 25 wt% Sb, 5 wt% Sn and 25 wt% Sn, 5 wt% Sb) were selected to be put in the museum as environmental reaction sensors on which electrolytic measurements were performed. Simultaneously, an adapted Oddy test* was set up to determine acidic environmental reactions on the selected alloys. Finally, it was possible to compare results by means of a cooperation with the Chemistry department of the University of Antwerp to perform measurements on atmospheric acid levels and particulate matter (Krupinska, Van Grieken, & De Wael, 2013) .

The results have shown that a large variation of alloys of the letters appear to be present in the different boxes, but also within each box and even in certain compartments of the boxes where the same characters of types were kept. Moreover, it did not seem possible to link any of the examined types to certain historical periods and no correlation was found between the actual type compositions and alloy descriptions from the time. Also, the recasting of types, possibly also partial, impede any possible correlation between original alloys that the printers may have used, and what is to be found as type metal alloys today.

From the research it became clear that the lead alloy letters containing high concentrations of Sb and low Sn were the most prone to severe corrosion. High levels and prolonged exposure to acid environments were found to be responsible for metal deterioration. In addition to this, it was remarkable that the letter boxes, which were made with a beech wood bottom, showed the most and strongest corrosion formation. This result was also obtained in the adjacent Oddy test, especially on the high Sb, low Sn Pb alloys. The conclusions were complementary to the observations of the museum objects. The first important result from this setup was the fierce corrosion reaction towards lead alloys from the beech wood, along with the expected corrosion reactions from the oak, multiplex and hardboard. Pine was affected the pure Pb and selected alloys least. The second significant result was the extremely strong corrosion reaction with a total decomposition of the Sb-rich alloys in formic acid environments, with or without the presence of acetic acids. Under the same conditions, pure Pb was corroded to a far less extent. This indicates that the presence of high Sb amounts in Pb alloys acts as a predominant factor in initiating extreme corrosion under strong formic acid conditions. These results were also the conclusion of a similar experiment at the University of Genova in 2013 (Ghiara, et al., 2014).

The environmental conditions in the museum were found to be an important part of the corrosion problem, as there are high organic acid levels present, originating from the abundant wooden building elements and furniture. This is shown in the results from the atmospheric sensors (coupons) that were placed in the museum as well as from the measurements made by the University Chemistry department.[1] It is however very difficult - if not impossible - to prevent this, as the main material for the museum interior and many of the machines and furniture is oak, which is historically related to the interior.

Since this initial research was conducted with only pure lead and two alloys with respectively 25 wt% Sb, 5 wt% Sn and 5 wt% Sb and 25 wt% Sn, more detailed information about the corrosion behaviour of Pb-Sb-Sn alloys was needed. In this chapter, a range of alloys corresponding to the majority of historical lead type metal compositions was used for the evaluation of corrosion development.

A selection of Pb-Sb-Sn alloys was exposed to ambient air and acidic environments. The corrosion development was assessed using colour changes (CIE-L*a*b*), UV-Vis spectrometry and gravimetric measurements. As a complementary test, electrochemical methods were applied, mimicking ambient and acidic environments. Finally, the corrosion products were evaluated on visual aspects, microscopically and with UV-Vis, Raman and X-Ray Diffraction.

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[1] Internal report, Storme et al. 2013

6.2 Experimental

6.2.1 Alloy selections

The choice of alloy compositions to perform the corrosion tests is identical to the set that was designed and produced in chapter 4. The selected set of alloys covers the ternary lead alloys compositional grid ranging from 0 to 20 wt% Sb and from 0 to 12 wt% Sn, in steps of 4 wt%, including an additional alloy of Pb 80, Sb 10 and Sn 10 wt%, resulting in a total of 16 alloys.

6.2.2 Atmospheric tests

The corrosion speed of metals and alloys depends on the corrosive atmosphere that is present, combined with the level of relative humidity (RH) and/or fluctuations in these values. Acetic and formic acid are the predominant air pollutants that trigger the corrosion on lead (Speerstra Joel, 2011). Ranges of carbonyl levels indoors are respectively 0.02-40.00 ppmv for acetic acid and 0.00005-1.00 ppmv for formic acid (Table 2.1) (Tétreault, et al., 2003). The levels of acetic and formic acid in the MPM were measured in 2011 and 2012, giving respectively 0.017-0.100 and 0.007-0.031 ppmv (see Table 2.2) (Krupinska, Van Grieken, & De Wael, 2013).

Previous research has shown that pure metals at high concentrations (ppm level) and at high relative humidity levels (RH >75%) often show high corrosion rates (Lafuente, et al., 2013). Some research on Pb-Sn alloys (Chiavari, et al., 2008) and on Pb-Sb alloys (Storme, Jacobs, & Lieten, 2013) (Ghiara, et al., 2014) at high RH levels shows in turn different results compared to pure metals.

To obtain test results for corrosion development at specified RH levels, stable environments are required. Such environments can be obtained experimentally using an RH-regulated glove box, an experimental set-up with controlled gas, air and RH regulated chambers (Speerstra Joel, 2011) or desiccators with RH stabilising salts (Astrup & Hovin Stub, 1990). Since no controllable glove box or experimental gas chamber set-up was available, no experiments with regulated RH levels were performed. The environments chosen for corrosion development on the lead alloys were (1) ambient air, (2) acetic Acid and (3) formic Acid.

A first series of tests (1) was executed in an ambient air environment to evaluate the tarnishing of the samples over a period of 10 weeks. The laboratory environment was only controlled for temperature (22.5°C ±2°C), while RH was measured with a thermohygrograph giving 50-75 % RH. No other data on the atmospheric conditions was collected.

The second series of tests was performed with the acidic environments (2, 3). The corrosive museum air climate was represented by using acetic and formic acid vapours. In order to obtain gas concentration variations in the corrosive atmospheres, different acidic concentrations were used as described in previous research (Schotte, 2007). The solution concentrations in the range of 30 to 0.3 mmol L^{-1}, however, showed in preliminary experiments that the corrosion reactions on the lead alloys appeared too slow within the available time-frame. For this reason, more concentrated solutions were chosen, namely 3 M, 0.3 M and 0.03 M. With these concentrations, corrosion development within a limited time-frame of one to four weeks was achieved.

All atmospheric experiments were executed in transparent 5.8 L desiccators, sealed air-tight. The acetic acid (AA) and formic acid (FA) solutions were 3 M, 0.3 M and 0.03 M respectively. The bottom part of each desiccator was filled with 10 vol% of the corrosive solution (580 ml), based on the results of the preliminary experiments and resulting in a saturated air environment inside the desiccator. The chosen time of exposure was one week for the 3 M solution, two weeks for the 0.3 M and four weeks for the 0.03 M solution. The corrosion development over time on the samples for each of the solutions was inspected visually. Every week the samples were weighed, spectroscopic measurements were executed and the corrosive solution was replaced.

6.3 Results

6.3.1 Exposure to corrosive environments, CIE-L*a*b*- and gravimetric evaluations

6.3.1.1 Ambient air environment

The visual appearance of the samples had already altered after a few days, resulting in a darkening and matting of the surface. In the following days and weeks, not much visual difference was noted until the end of the experiment after a 10-week exposure time (Fig. 6.2-Fig. 6.4). All samples had a shiny mid-grey aspect at the start; the lower row in the images reflects a shadowed part in photographing. After a period of six weeks exposed to the air the darkened and matt surfaces also showed a yellowing on the Pb-Sb alloys. After 10 weeks of exposure matt grey again became the dominant aspect of the samples.

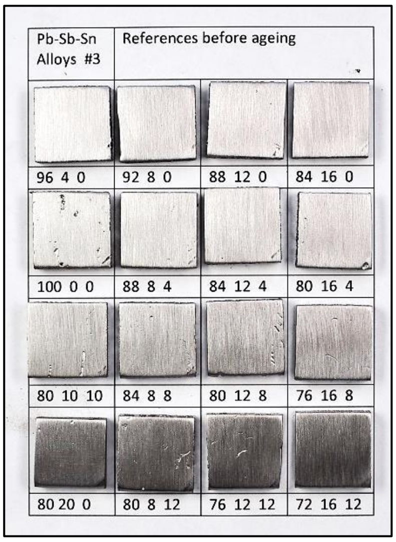


Fig. 6.2: Samples at the start of the experiment.

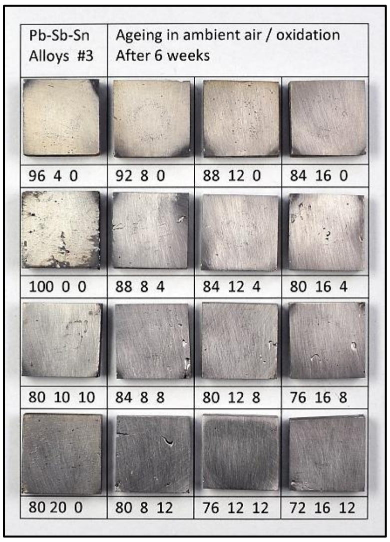


Fig. 6.3: Aspects after a period of six weeks' exposure to air.

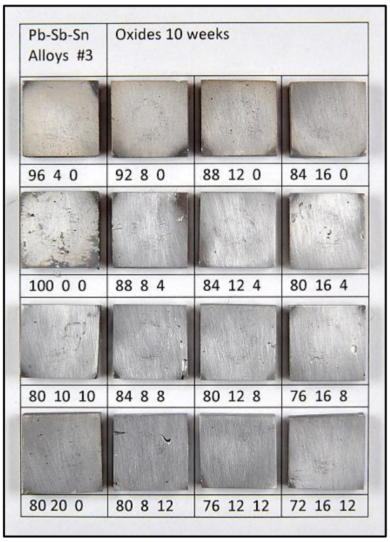


Fig. 6.4: Final aspect after 10 weeks' exposure to air.

All alloys show a rapid tarnishing after the first week, with a clear change in colour (Fig. 6.5). After the first week, no further significant colour changes (CIE-L*a*b* evaluation, expressed as ΔE) were determined. The alloys Pb-Sb (without Sn) show the greatest changes after one week, with values between ΔE 2.8 and 5.0. In the next weeks, all Pb-Sb alloys develop higher values up to ΔE 6.7 – 9.2 after 10 weeks of exposure. Pure lead and Pb-Sb-Sn alloys in turn show smaller changes and all stay within the range of ΔE 2.1 - 4.3 after 10 weeks of exposure.

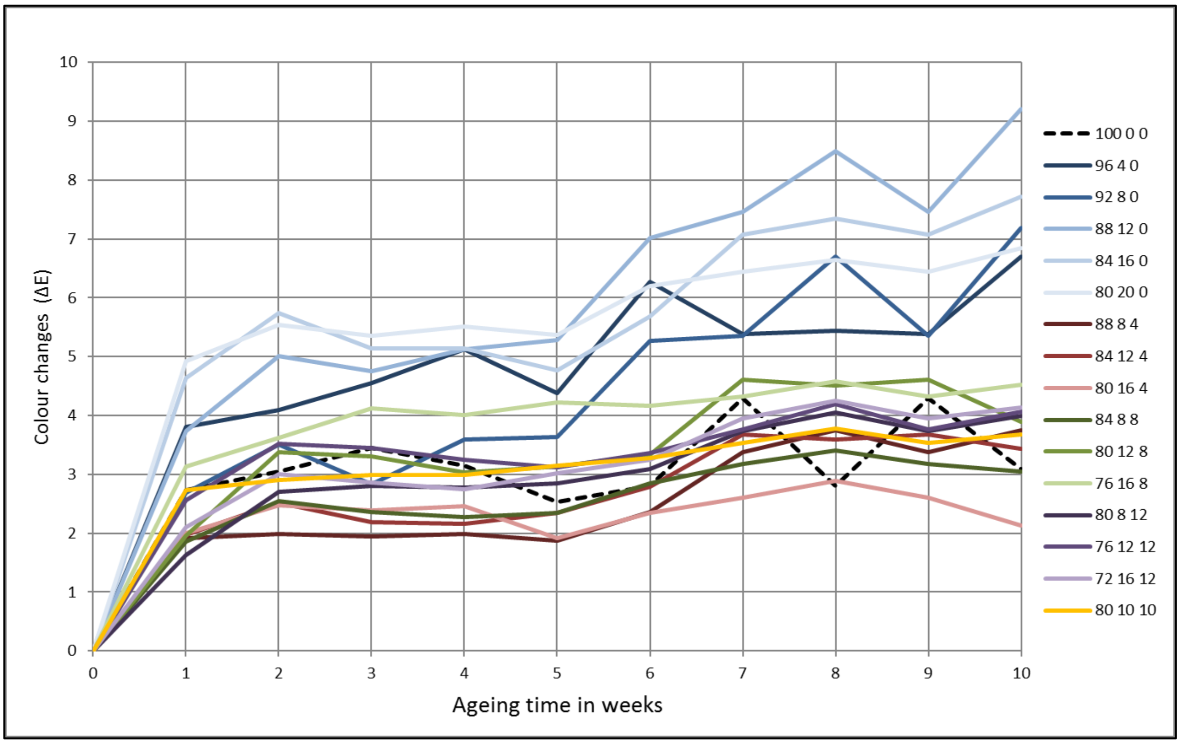


Fig. 6.5: Colour change results during 10 weeks' exposure of the alloys to ambient air.

The CIE-L*a*b* values mainly wrap up the L* values (Fig. 6.6) as there is a drop noticed for all alloys, but the strongest for the Pb-Sb alloys (c. 75 to c. 68) compared to the Pb-Sb-Sn alloys (c. 77 to c. 74). The specific a* values (Fig. 6.7) differ only slightly with readings between 0.8 and 1.4. The b* values (Fig. 6.8) show a stagnation for Pb and the Pb-Sb-Sn alloys (c. -0.5), whereas the Pb-Sb alloys show a dramatic rise in values for the first week and as a final result (from c. -1.2 to +1.5), due to a slight yellowing of the surface. As a conclusion, the separate L* and b* values indicate the greatest differences in the colour changes of the samples exposed to ambient air.

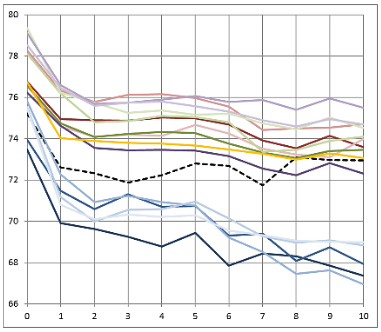


Fig. 6.6: L* values.

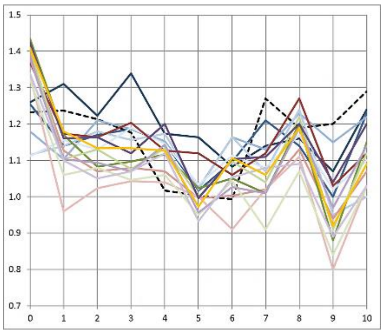


Fig. 6.7: a* values.

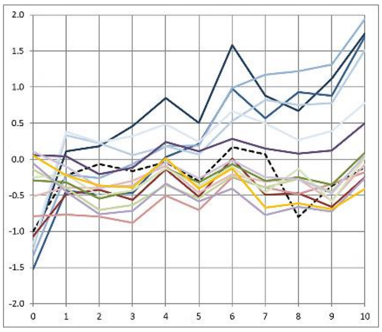


Fig. 6.8: b* values.

Gravimetric evaluations did not support the observations. The samples that weigh about 10 grams each had too small weight changes that stayed within the error limits of the balance (0.003 g).

6.3.1.2 Acetic acid environments

The atmospheric corrosion tests were executed with a 3 M AA solution first during one week of exposure. This resulted in a large variation in corrosion formation, due to condensation on the samples. Some samples became covered with white corrosion products while others became black (Fig. 6.9). As a result, the CIE-L*a*b* results did not indicate a relationship between corrosion formation and alloy composition.

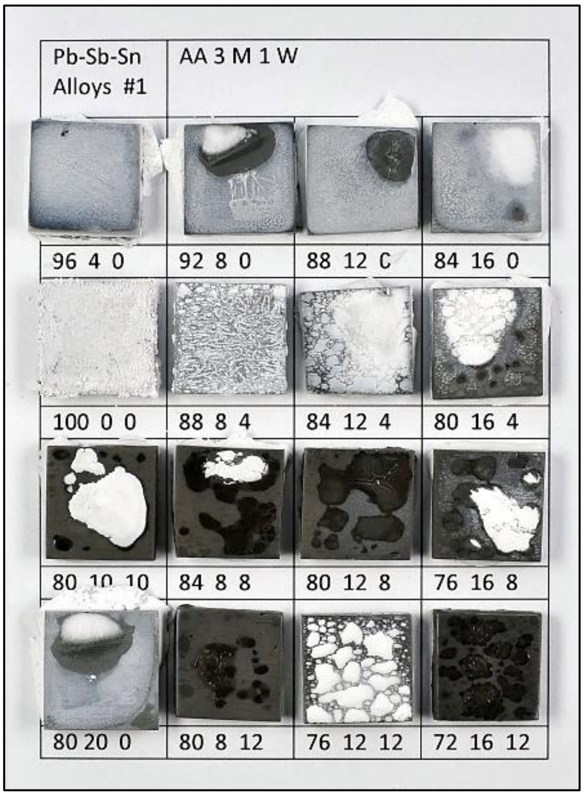


Fig. 6.9: Corrosion formation after one week of exposure to a 3 M acetic acid solution.

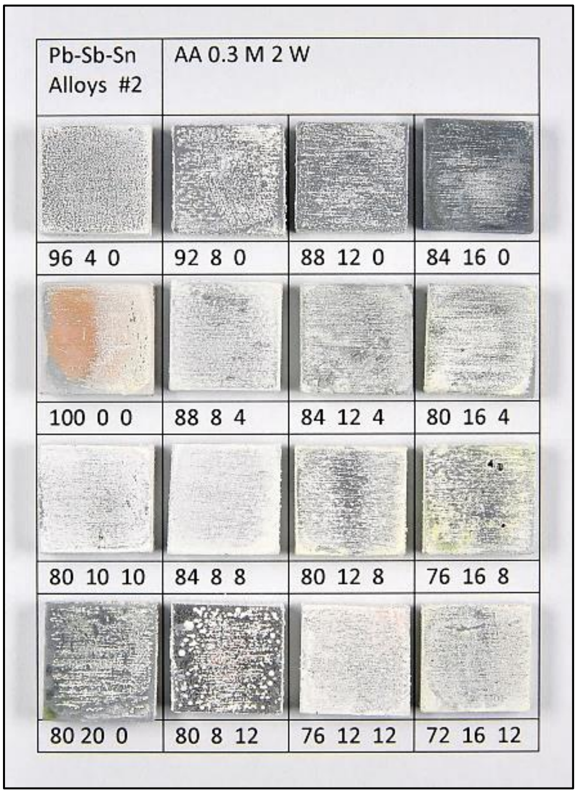


Fig. 6.10: Results after two weeks of exposure to 0.3 M saturated air

The exposure to the AA 0.3 M saturated air environment for two weeks did result in uniform corrosion formation, except for Pb where apparently a pinkish coloured corrosion was formed (Fig. 6.10). As for the stronger concentration, there were also no consistent results to be drawn from the CIE-L*a*b* values. The pinkish product on Pb might be explained as the occurrence of lead acetate oxide hydrate (colourless or white), litharge (red), massicot (yellow) and plumbonacrite (colourless, white or grey), as also seen in the experiments with acetic acid environments on lead samples representing organ pipes (Speerstra, J., 2011). It is however not clear why it has not developed on any of the alloys.

Exposure to the 0.03 M AA saturated air shows a more consistent development of corrosion products compared to the higher concentrations. The first week of exposure shows the greatest colour changes (ΔE values, Fig. 6.13) for the Pb-Sb alloys from 17.9 to 20.9, pure Pb 13.4 and the Pb-Sb-Sn alloys 7.6-15.7. From the first week until the end of the test at four weeks, almost no further changes were noted and all results concentrate between 10-20 ΔE. The Pb-Sb group without Sn, which corroded the fastest at the beginning, even seems to decrease towards the end of the four week exposure period. The stronger colour changes compared to the more concentrated 0.3 M AA solution could be explained by a higher concentration of CO_2 in the desiccator since less acid is present in the air volume.

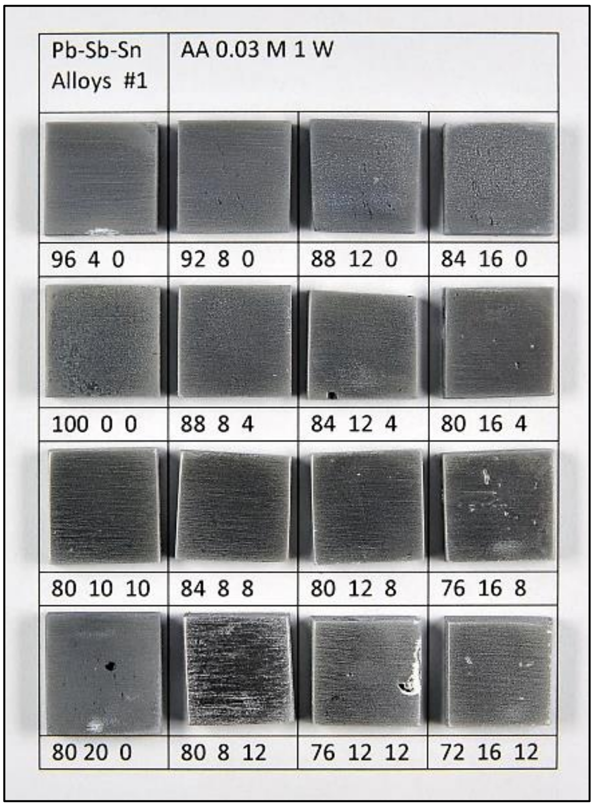


Fig. 6.11: Visual appearance after one week of exposure to the 0.03 M AA saturated air.

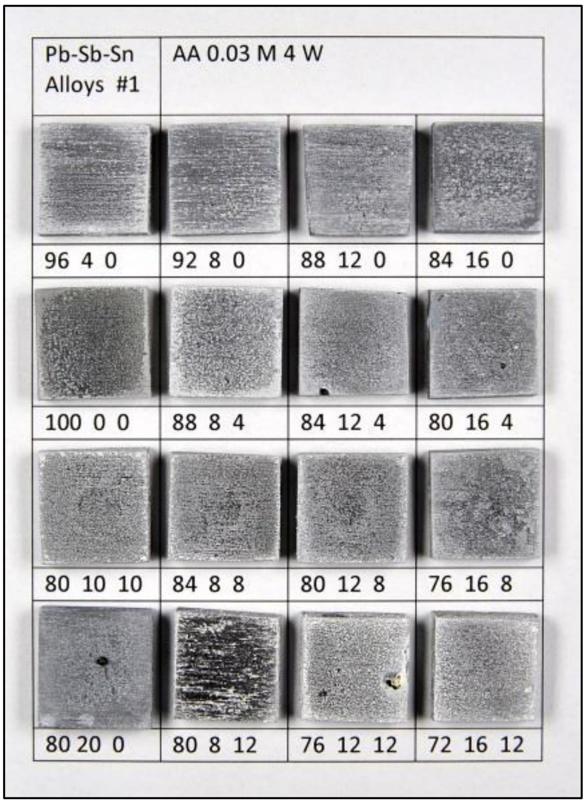


Fig. 6.12: Visual appearance after four weeks of exposure to the 0.03 M AA saturated air.

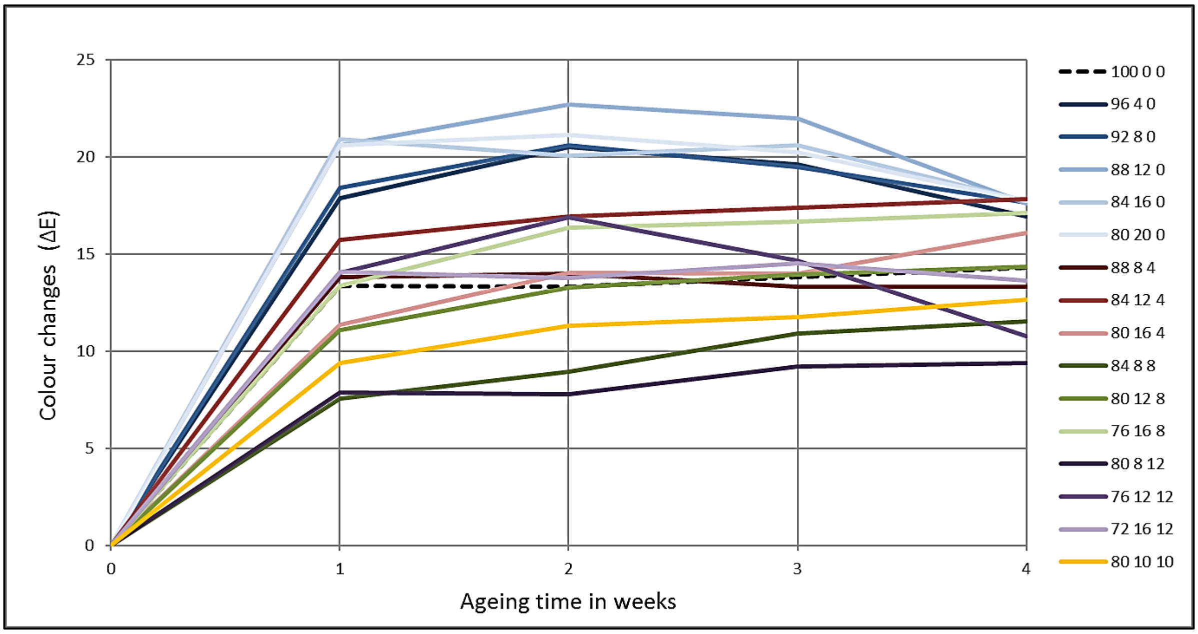


Fig. 6.13: Colour change results during a four-week exposure to the 0.03 M AA saturated air.

For a better understanding of the CIE-L*a*b* results, each value is evaluated separately (Fig. 6.14 - Fig. 6.16; axis and legend as in Fig. 6.13). Here, a grouping in the results is present in the L* and b* values whereas the Pb-Sb alloys deflect from Pb and the Pb-Sb-Sn alloys. All L* values decrease, with the Pb-Sb alloys fastest and clearly separated from the Pb and the Pb-Sb-Sn alloy group; for the a* values, all alloys show a decrease although the difference is not significant (from c. 1.3 to c. 0.5); and for the b* values only after the first week of exposure is a stronger decrease for the Pb-Sb alloys noted (from c. -1 to c. -3.5) as opposed to a minor decrease for the Pb-Sb-Sn alloys (from c; +0.5 until c. -1). Pure Pb and the alloy 80-8-12 stay positive (c. +1).

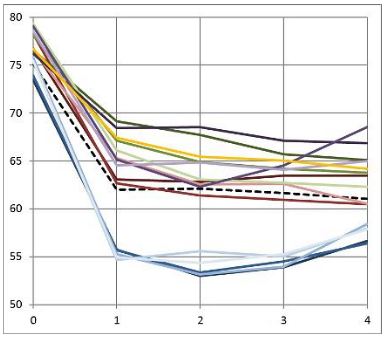


Fig. 6.14: L* values.

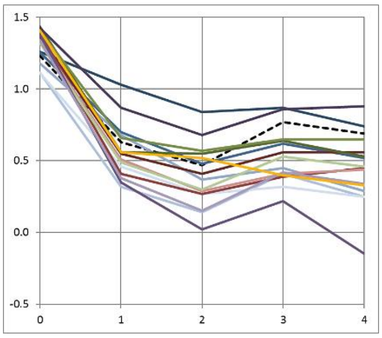


Fig. 6.15: a* values.

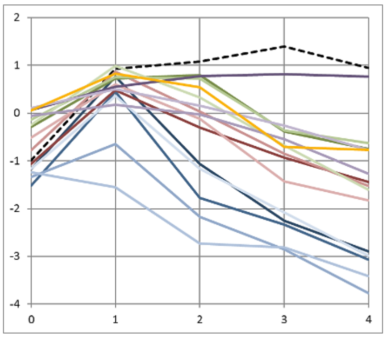


Fig. 6.16: b* values.

From the results, it can be concluded that the ΔE values and their relationship to the alloy compositions after one week's exposure to a 0.03 M acetic acid saturated air environment are very similar to the results after four weeks of exposure. The stronger corrosion development due to the concentrations of Sb on the one hand and the inhibiting effect of Sn additions on the other is clearly visible in Fig. 6.17, giving lower b* values compared to the Pb-Sb alloys. In conclusion, it can therefore be suggested that the exposure time could be restricted to one week.

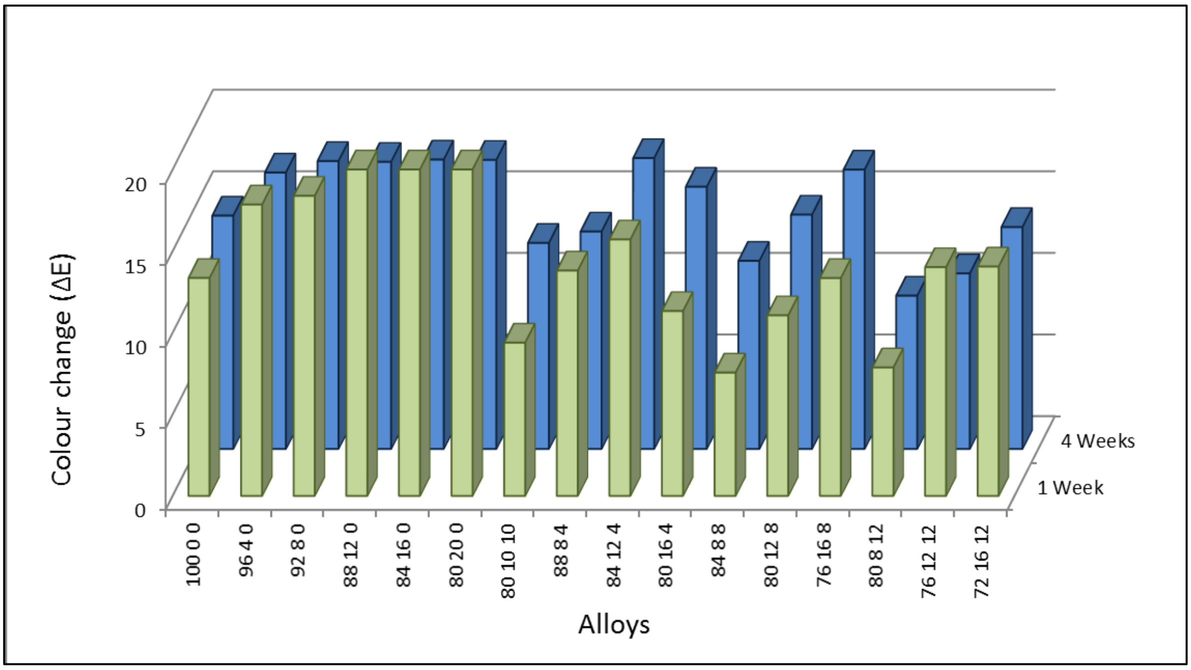


Fig. 6.17: Results for the ΔE values of the series of alloys exposed for one and four weeks to the 0.03 M AA saturated air.

The gravimetric results from the samples exposed for one week to the 3 M acetic acid saturated air show the strongest increase for the alloys without Sn. The group of Pb-Sb alloys shows the highest weight gain (0.7-1.0 %) compared to pure Pb (0.6 %) and the Pb-Sb-Sn alloy group (0.1-0.7 %), with one exception for the alloy with 16 wt% Sb and 4 wt% Sn (also 1.0 %). This weight gain is not related to the visual appearance of the corrosion formation, which is highly varied (Fig. 6.9).

Gravimetric results for the 0.3 M saturated air environment show a steady increase for all alloys without much differentiation between the alloys with or without Sn. The weight increase after two weeks of exposure is about 20 % compared to the 3 M saturated air, ranging between 0.11 % - 0.23 %.

The 0.03 M solution environment show no clear differentiation in weight gain between the alloys. Values range from 0.03 % to 0.07 % with one exception at 0.13 % (Pb-Sb-Sn 76-12-12). The average weight increase after four weeks of exposure, however, is again about 20% compared to the 0.3 M saturated air.

6.3.1.3 Formic acid environments

Results from the 3 M FA saturated air show visually a direct relationship with the Sb content of the alloys (top row and left bottom corner in Fig. 6.18). Increasing amounts of Sb show a stronger matting and darkening of the sample surfaces. The Sn-containing alloys have a much lighter grey appearance.

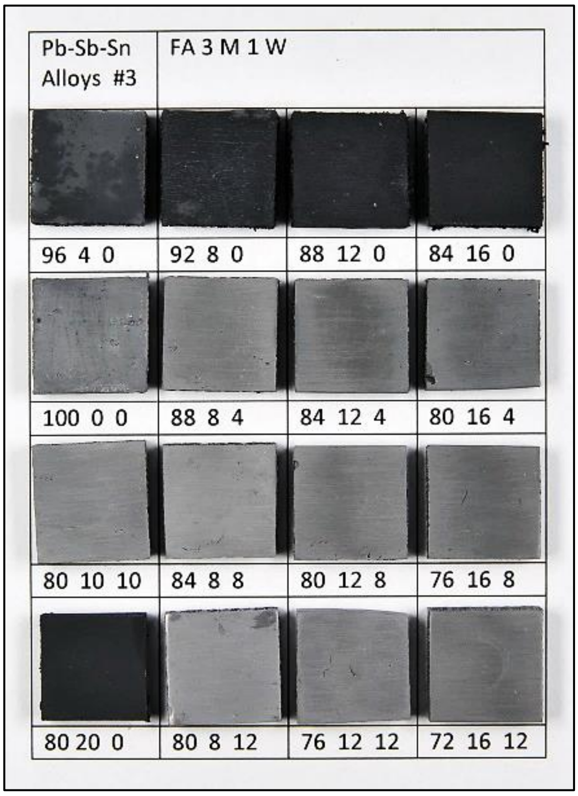


Fig. 6.18: The alloys after one week's exposure to the FA 3 M environment.

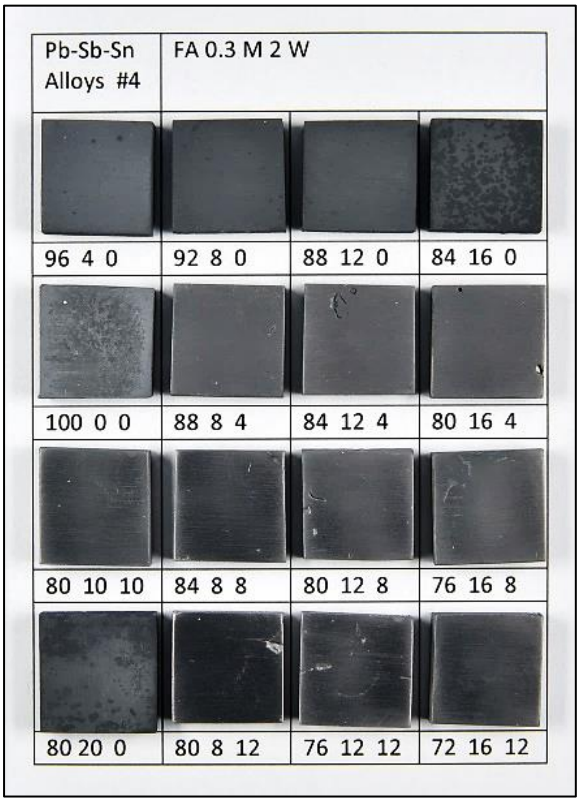


Fig. 6.19: Two weeks of exposure to 0.3 M FA saturated air.

The ΔE values (Fig. 6.20) of the Pb-Sb alloys are in the group with the strongest increase in values: 4 wt% Sb has a ΔE of 30.0 and higher Sb contents range from 35.3 to 37.8. Pure Pb has a ΔE of 24.5 and the Pb-Sb-Sn alloys (with 8-16 wt% Sb) have values from 18.7-31.2 ΔE.

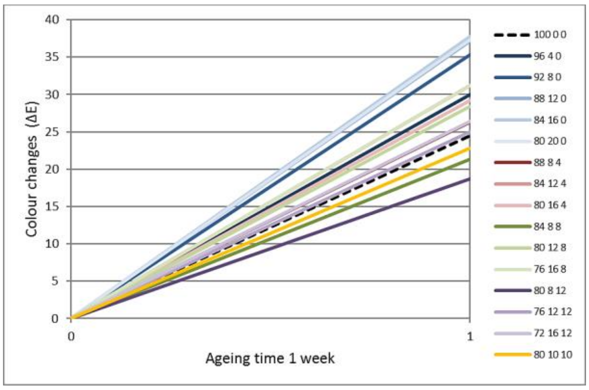


Fig. 6.20: Colour changes of the samples after one week in a 3M FA saturated air.

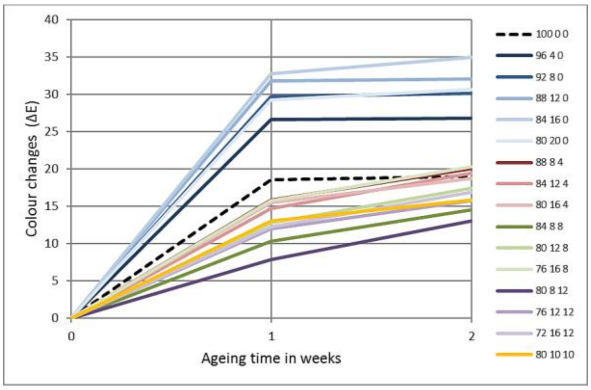


Fig. 6.21: Colour changes over two weeks in a 0.3 M FA saturated air environment.

In the 0.3 M FA saturated air (Fig. 6.21), the Pb-Sb alloy group reacts most strongly with ΔE values between 27 and 35. The colour change for this group is nearly as high as in the 3 M saturated air (30-38). Pure Pb shows a medium reaction (19) compared to the alloys containing Sn, which have the lowest ΔE values after one week (8-16). After two weeks of exposure, the results for the Pb-Sb-Sn alloys show values between 13 and 21. It is significant that Pb and the Pb-Sb alloys show a stagnation of colour change after the first week, indicating a slower reaction to the corrosive atmosphere.

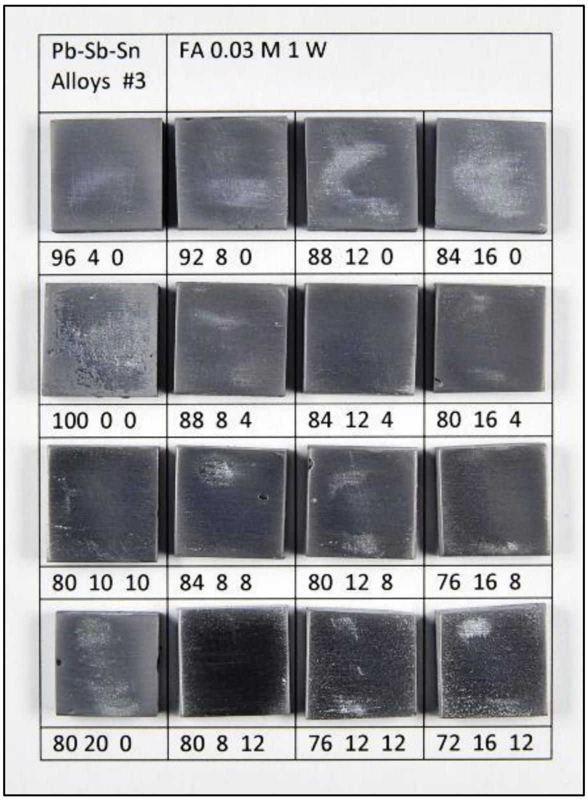


Fig. 6.22: Exposure to the 0.03 M FA saturated air, after one week of exposure.

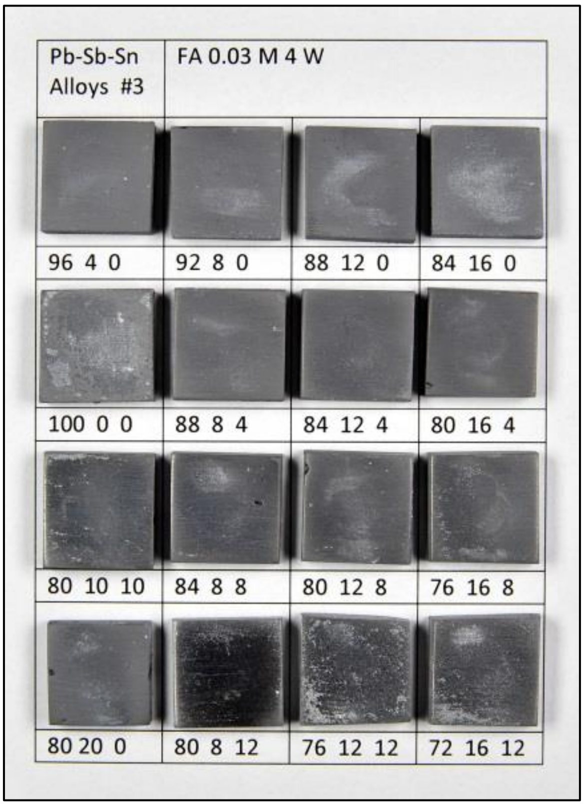


Fig. 6.23: Results of four weeks' exposure to the 0.03 M FA saturated air.

For the group alloys exposed to 0.03 M FA saturated air, the results show a rapid visual darkening of the surfaces after the first week, only slightly changing closer to the total exposure time of four weeks. (Fig. 6.22-Fig. 6.23). This is also reflected in the ΔE values (Fig. 6.24).

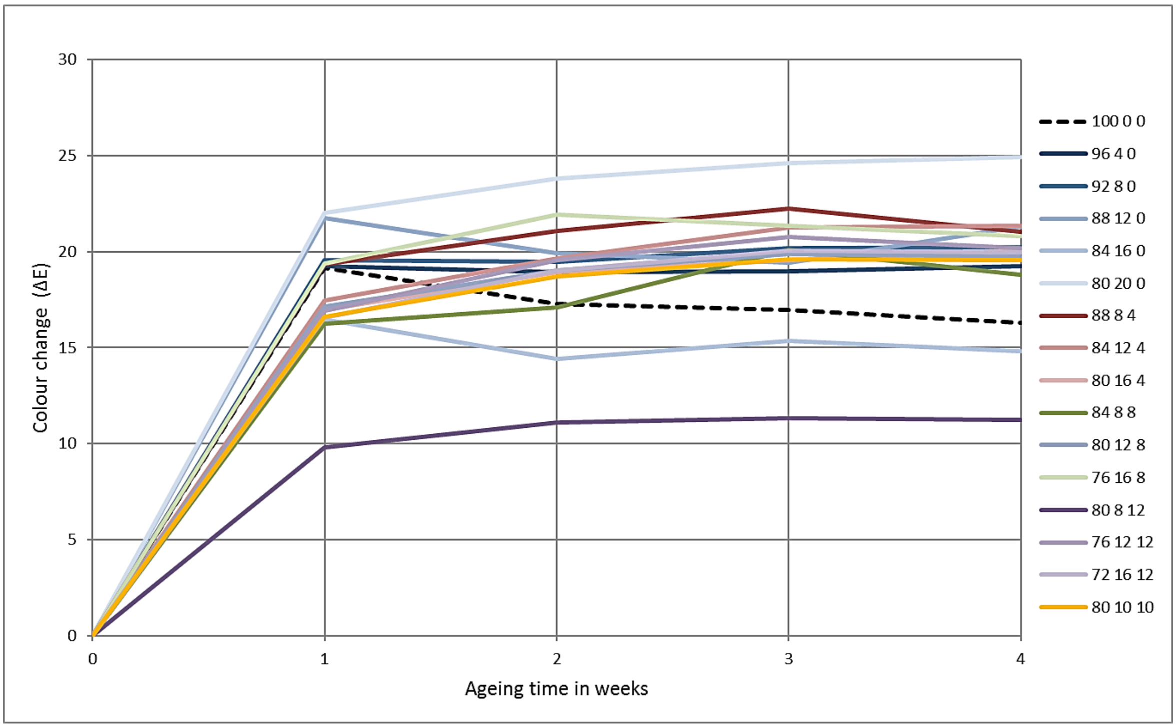


Fig. 6.24: Colour changes during four weeks' exposure of the alloys to a 0.03 M AA atmosphere.

Although the CIE-L*a*b* and the L* values for the 0.03 M solution (Fig. 6.25) show no distinction between the alloys with or without Sn, the separate a* and b* values do show a split between the two groups (Fig. 6.26-Fig. 6.27) with respectively fewer red and more blue colour values for Pb and the Pb-Sb alloys as opposed to the Pb-Sb-Sn alloys. Axis and legends are identical as in Fig. 6.24.

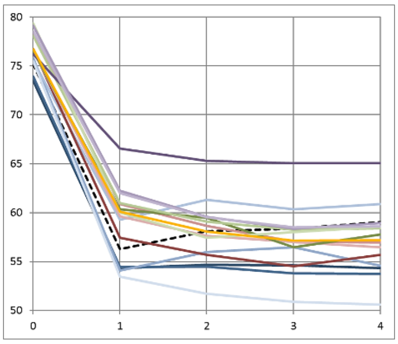


Fig. 6.25: L* values.

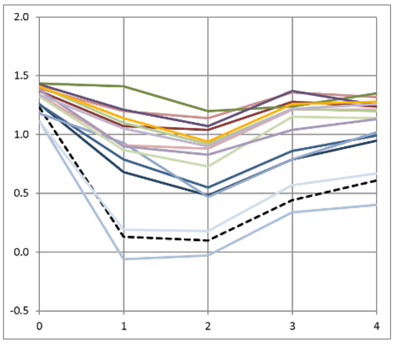


Fig. 6.26: a* values.

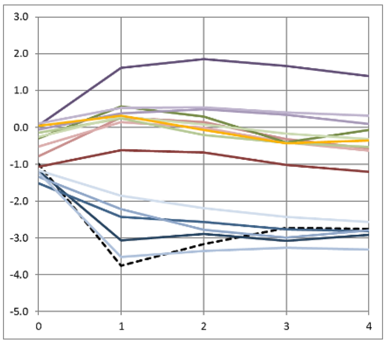


Fig. 6.27: b* values.

Results of the CIE-L*a*b* measurements show a relationship between the colour change and the concentration of the solution in the desiccator where the samples are exposed to the formic acid atmosphere. The results for all solution concentrations show after one week respectively for the 3 M FA a range of ΔE values between 19-38; the 0.3 M solution gives values in the range of 9-33 and the 0.03 M shows results between 10-22 ΔE (Fig. 6.28). The relationship between corrosion development and Sb content for the alloys with and without Sn is shown most clearly for the 3 M FA saturated air.

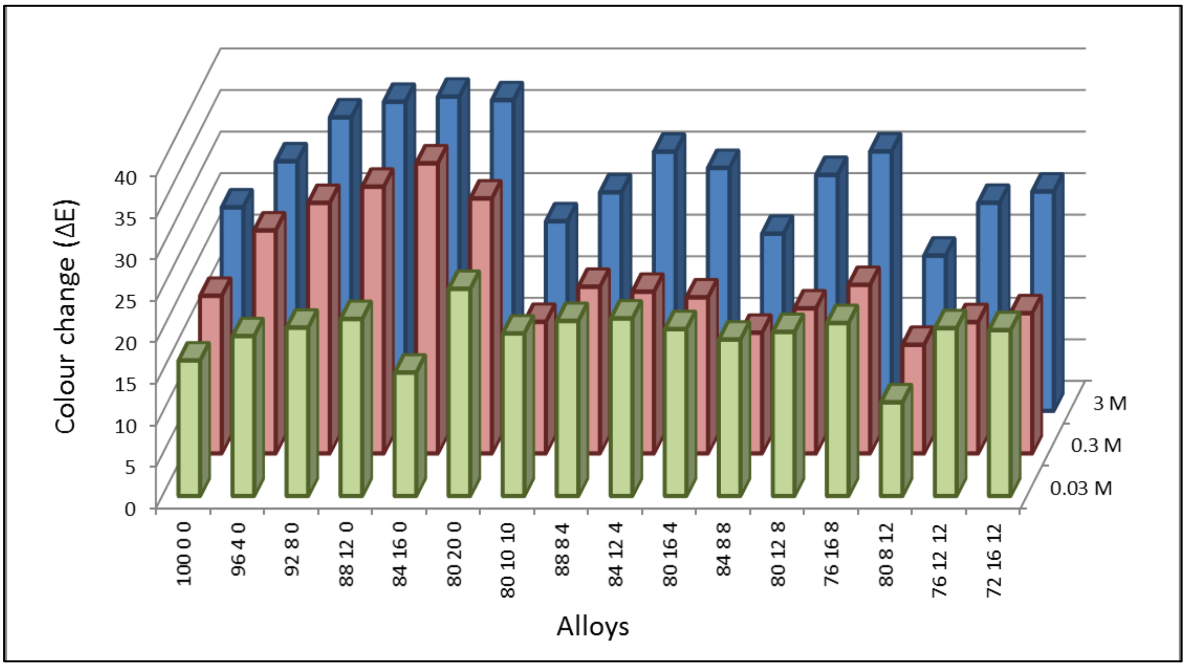


Fig. 6.28: ΔE values after 1 week of different FA saturated air concentrations.

When comparing the colour changes of the samples that were exposed to the different formic acid environments, some trends are to be distinguished. Firstly, the ΔE values increase with higher concentrations of formic acid. For the 0.03 M solution an average of about 10-20 ΔE is noted, for the 0.3 M that is about 10-30 and for the 3 M solution, 20-40 ΔE is recorded (Fig. 6.28). Secondly, with the increase of Sb-levels in the alloys, the ΔE value rises as well. This is the case for all alloys, with the highest values for the Pb-Sb alloys without Sn and slightly lower values for the Pb-Sb-Sn alloys. The clearest relationship between acid concentration, Sb/Sn content in the alloys and corrosion development is determined with the 0.3 M and 3 M solution.

Gravimetric changes of the samples from one week of exposure to the 3 M FA saturated air clearly show a direct relationship with the Sb content. The highest weight increase is noted for the Pb-Sb 80-20 wt% alloy (0.60 %), decreasing with respectively Sb 16 wt%, 12 and 8, down to 4 wt% (0.15 %). Pure Pb and the Sn containing alloys all stay well beneath these values with weight changes below 0.10 %. The relationship with the visual appearance is clear, as shown in Fig. 6.18. The weight changes on the samples from two weeks exposed to the 0.3 M and four weeks to the 0.03 M saturated air, the weight changes were respectively lower than 0.06 % and 0.02 %, which is near or below the error range of the balance and gave no conclusive data. They are therefore not applicable.

6.3.1.4 Discussion on the colour measurements

The relation between colour changes and the lead alloy compositions with variated Sb and Sn concentrations are expressed as ΔE values from the CIE-L*a*b* results, presented in Fig. 6.29-Fig. 6.32 by the series that gave the most distinct results, i.e. for ambient air after 1-10 weeks of exposure, for the 0.03 M AA solution after one week of exposure and finally for the 3 M FA saturated air also after one week. This choice is supported because even though the weaker solutions had a longer total time of exposure, all CIE-L*a*b* values reached their maximum and most distinctive results after one week.

Even considering that the results of the ambient air environment are higher after 10 weeks of exposure (Fig. 6.29), the colour change trends between the alloy groups are already visible after one week of exposure (Fig. 6.30).

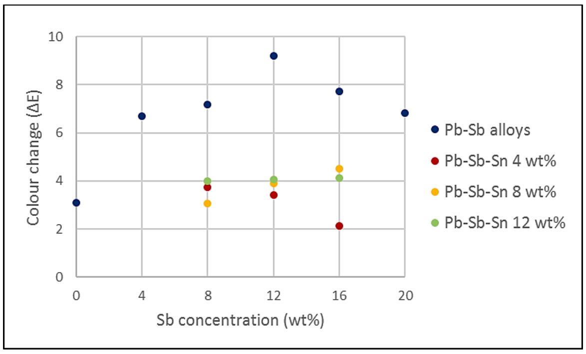


Fig. 6.29: Colour changes after 10 weeks of exposure to the ambient air environment.

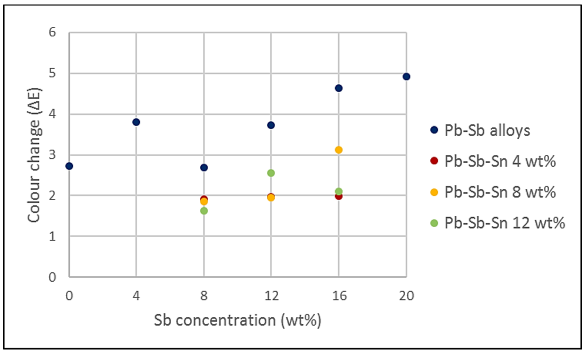


Fig. 6.30: Colour changes after one week of exposure to the ambient air environment.

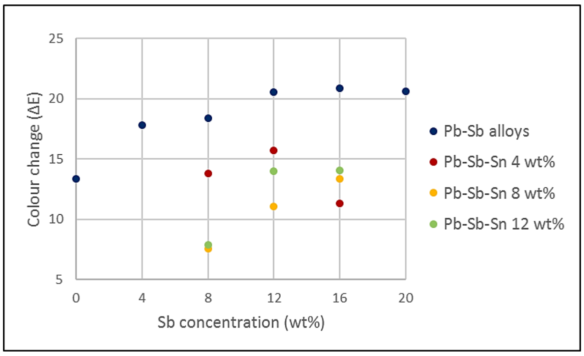


Fig. 6.31: Colour changes after one week of exposure to the 0.03 M AA environment.

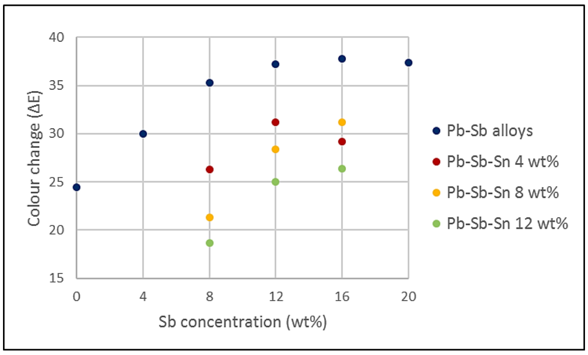


Fig. 6.32: Colour changes after one week of exposure to the 3 M FA environment.

There are however differences in values between the stronger and weaker solutions. Ambient air probably has the lowest concentration of corrosive elements in the air and gives a maximum reading of ΔE 5 after one week. The AA environments show maximum values from 21 to 36 for respectively the 0.03 and 3 M solutions. The solution of 0.3 M is deviant because of its lower values and there is no clear reason for this. After one week of exposure the FA environments show maximum values of 23, 33 and 38 for respectively the 0.03 M, 0.3 M and 3 M solutions. In most cases the subsequent weeks of exposure do not deliver significant different data. It can be concluded from these experiments that the evaluation with CIE-L*a*b* is effective for all concentrations after one week of exposure of the samples, especially for the Pb-Sb alloys that react strongest to the three tested atmospheres.

Further investigations with Pb-Sb alloys could help establish a relationship between the CIE-L*a*b* values and the corrosion mass over a certain period of time. This could be useful for the application and evaluation of metal coupons for monitoring the air corrosiveness in museum exhibition rooms, storage rooms, showcases or other environments. An additional advantage of fast-corroding sensors and an easy evaluation system could lie for instance in the application of large numbers of metal sensors throughout a museum, in order to locate possible VOC sources.

6.3.2 Corrosion development and characterisation using UV-range spectroscopy

6.3.2.1 UV-Vis spectroscopy introduction

In previous chapters, CIE-L*a*b* colour changes were recorded to evaluate the corrosion development on samples exposed to ambient air and accelerated acidic environments. The spectra provided information in the visible light spectrum (380-780 nm), but apparently also in the UV-Vis range (200-380 nm). This chapter will look at these specific spectra in relation to the corrosion products that have been formed on the surface in the different environments.

UV-Vis absorbance spectrometry and Specific UV Absorbance (SUVA) in transmission is widely used for the identification of organic molecules, most commonly in solutions. Absorbance usually ranges from 0 (0% absorbance) to 2 (99% absorbance). Diffuse Reflection Spectroscopy (DRS) is used to collect spectra of powders and rough surfaces. An integrating sphere was used for the diffusion of the illuminating rays on the sample surface, while the spectra were collected at an angle to the illumination optics. It should be noted that UV-Vis measurements in absorbance mode may be subjected to surface roughness, grain sizes, transparency and reflective capacities. The samples were glass-bristle brush cleaned before each corrosion experiment. Hence, the reference spectra were also taken from this brushed, non-corroded surfaces.

The visible light spectra give mainly white or grey variations (Fig. 6.33) on lead alloys. For corrosion development and identification, the UV-range spectra were used in this chapter. The results of the measurements are given specifically in the spectral range of 200-400 nm (Fig. 6.34). In this graph, an example of the absorbance values (A) and peak formations in the UV-range is demonstrated for Pb-Sb alloys before ageing and after an exposure of one week to a 3 M acetic acid environment.

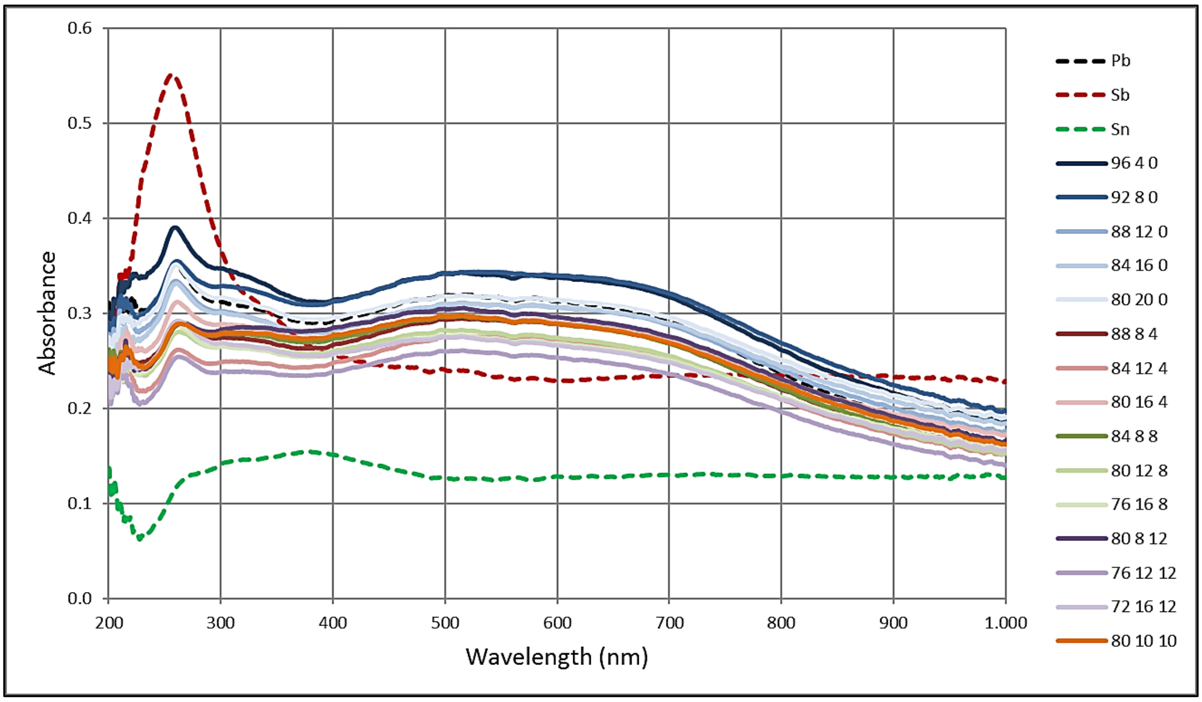


Fig. 6.33: Reference absorbance spectra of Pb, Sb and Sn (dotted lines) and the Pb-Sb and Pb-Sb-Sn alloys (full lines), before ageing.

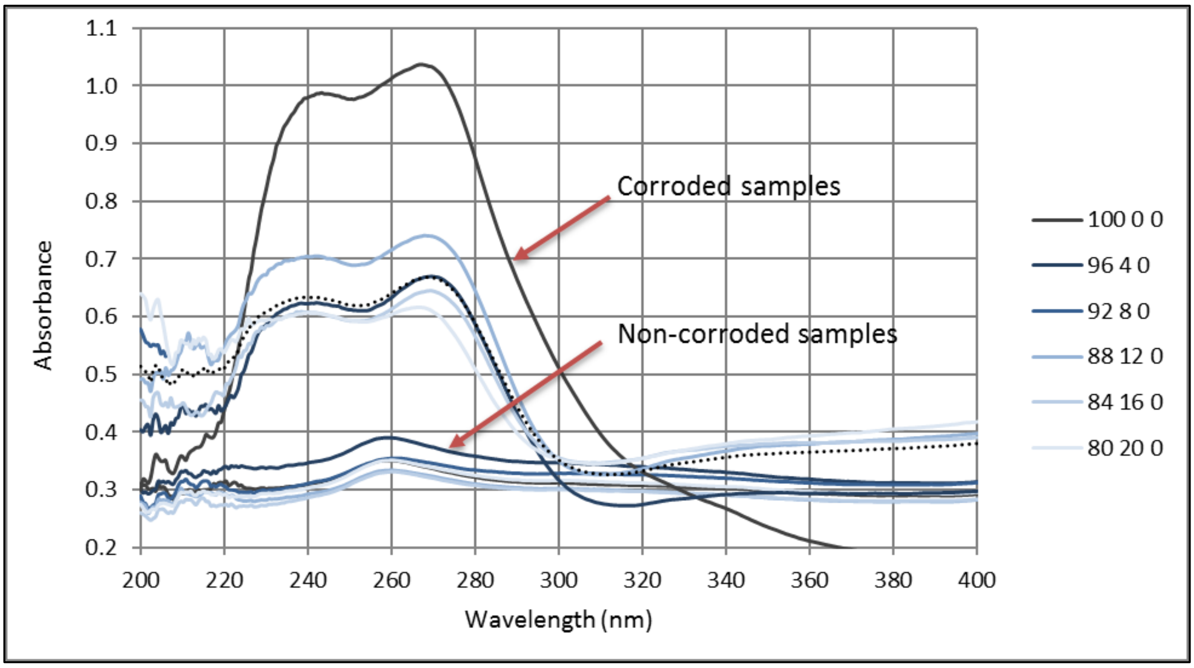


Fig. 6.34: Absorbance spectra of blank and corroded Pb and Pb-Sb alloys. The dotted line indicates the average spectrum of the Pb-Sb alloys.

6.3.2.2 Ambient air environment

Newly prepared Pb, Sb and Sn samples have bright reflective surfaces, as can be seen on Fig. 6.33 in the visible light spectrum (low absorbance in the 400-800 nm range). In the UV-region Sb shows a very distinctive peak at 260 nm (0.55 A), where Sn has very low absorbance values (about 0.13 A) with a dip around 225 nm. Pure Pb has a more grey appearance together with all of its alloys and gives absorbance values of about 0.30 A in the visible light range. Generally, the absorbance spectra for the Pb-Sb alloys show higher values compared to the Pb-Sb-Sn alloys.

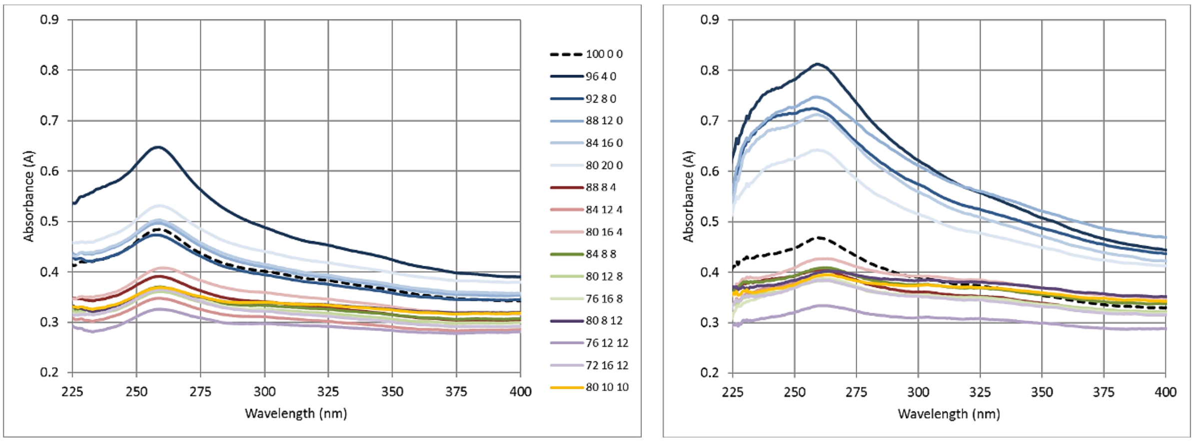


Fig. 6.35: Absorbance spectra after one week of exposure to ambient air on the left; on the right the absorbance spectra after 10 weeks of exposure to ambient air.

After the first week of ambient air exposure, there is a significant increase in peak height for Pb and the Pb-Sb alloys, with the largest increase in the alloy of 4 wt% Sb, from 0.39 to 0.65 A (Fig. 6.35). Other Pb-Sb alloys increase to around 0.50 A while the alloys containing Sn only show a small increase and are grouped between 0.33 and 0.41 A.

After three and six weeks, a further rise in the Pb-Sb group is noted with a continuous increase for the 4 wt% Sb but a stronger increase for the 8 wt% Sb. Pure Pb and the group with Sn contents shows a status quo in absorbance values. In the following weeks, the Pb-Sb alloys further increase in absorbance values to a distinct definition from the pure lead and the Pb-Sb-Sn alloys. The highest absorbance value is noted for the lowest Sb content (Sb 4 wt%, 0.82 A), gradually decreasing for the highest Sb content (Sb 20 wt%, 0.64 A). The reason for this is not fully clear and seems to be contradictory to the CIE-L*a*b* results, but this could be due to the lesser Pb-surface and the subsequent corrosion product development that there is less absorbance for the 20 wt% Sb alloy. As seen on the metallographic images of the Pb alloys with high Sb concentration, large Sb grains are present, which do not corrode in air.

Tin inhibits oxidation and the results show that the alloys with the highest Sn concentrations are positioned amongst the lowest absorbance spectra (Fig. 6.35). However, it is remarkable that alloy Pb-Sb-Sn 76-12-12 (purple line) has the lowest absorbance of all and not 80-8-12 (dark purple line), with a lower concentration of Sb. The reason possibly lies in the fine eutectic microstructure of alloy 76-12-12 as opposed to larger Pb-rich grains in 80-8-12 that are more prone to oxidation.

Corrosion of the lead alloys in an ambient air atmosphere gave distinctive results in the increase of the spectral absorbance values for the Pb-Sb group as opposed to the Pb-Sb-Sn group. The darkening of the Pb-Sb alloys compared to Pb and the Pb-Sb-Sn alloys did provide results from the visible spectrum, as the CIE-L*a*b* values showed in the previous chapter. Using the UV-range spectra however, and more specifically the 255-260 nm range, these changes appear to be much larger, from 0.38 A up to an absorbance of over 0.80, showing an increase of over 200%. Especially, the Pb-Sb 94-4 wt% alloy seems to corrode the fastest (after one week, Fig. 6.35), whereas the other Pb-Sb alloys follow with increasing absorbance values after 10 weeks of oxidation. In the last weeks of exposure, an additional peak increase in the 240 nm range is noted. Pure lead stayed virtually unchanged. Detailed spectra for 1, 3, 6 and 10 weeks exposure can be consulted in the attachments.

6.3.2.3 Acetic acid environments

The corrosion layers, formed in the 3 M AA saturated air have a very varied visual appearance (Fig. 6.9). A selection of the most significant alloys is shown at microscopic level (Fig. 6.36), i.e. pure Pb, Pb-Sb 80-20, Pb-Sb-Sn 80-10-10 and Pb-Sb-Sn 80-8-12 wt%. This selection represents pure lead, the alloy with the highest concentration of only Sb (20 wt%), the sub-binary Pb-Sb-Sn eutectic alloy (80-10-10) and finally the alloy with the highest concentration of Sn (12 wt%) and the lowest Sb (8 wt%).

Despite the fact that the visual results of the corrosion are very varied, clear spectral results with distinctive peaks at 240 and 266 nm ±2 nm (Fig. 6.37) are determined. Corroded Pb shows the highest absorbance (up to 1.0 A), followed by the Pb-Sb-Sn alloy group (up to almost 0.8), and finally the Pb-Sb group with least absorbance (0.6-0.7 A). The surface of Pb does indeed visually show the most white corrosion compared to the alloys, which have more dispersed corrosion formation.

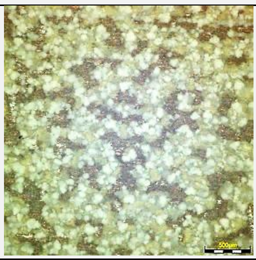
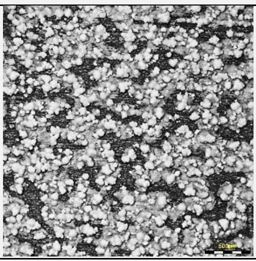
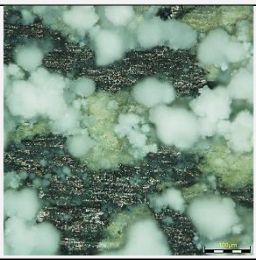
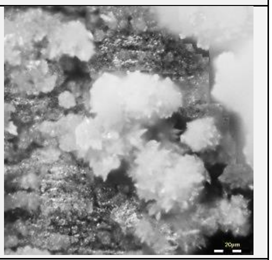
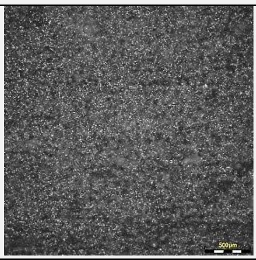
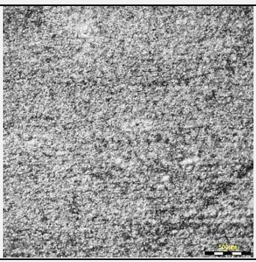
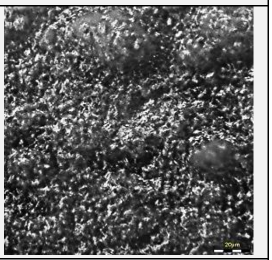
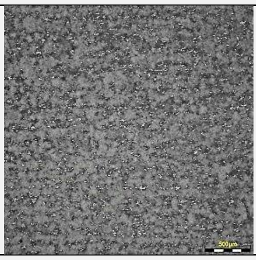
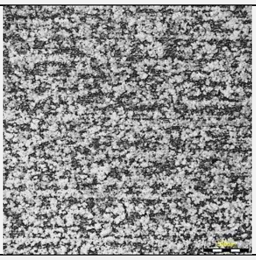
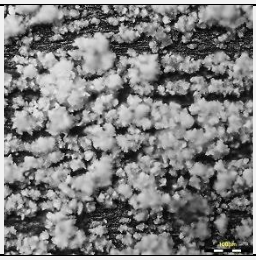
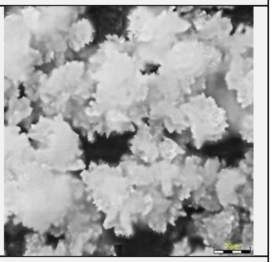
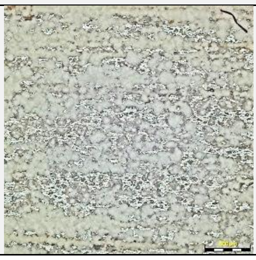
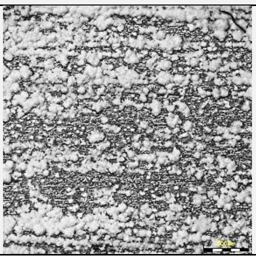
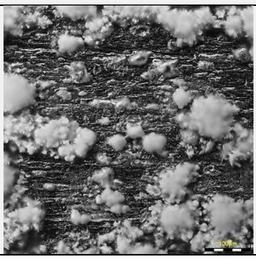
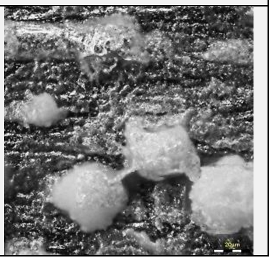
AA **0.3 M**	**100x BF** Scale bar 500 µm	**100x DF** Scale bar 500 µm	**500x DF (BF for Pb)** Scale bar 100 µm	**2000x DF** Scale bar 20 µm
Pure Pb				
Pb-Sb 80-20				
Pb-Sb-Sn 80-10-10				
Pb-Sb-Sn 80-8-12				

Fig. 6.36: Microscopic images from four lead and lead alloys, exposed to an 0.3 M AA environment.

Four alloys have not formed a white corrosion product at the centre of the sample (Fig. 6.9) where the spectra is measured. For these samples this resulted in a deflected spectral line, indicated as Average 1 (Av.1 in Fig. 6.37). The absorbance value is however similar to the Pb-Sb-Sn alloys that did develop white corrosion (Av.2, 0.7-0.8 A), showing a similar curve line form in the peaks region 240-266 nm. This indicates that the UV measurements record peaks related to the corrosion product, independent of the surface colour.

The samples from the 0.3 M AA saturated air give a broad spectrum rise with absorbance values of about 1.0-1.25 A between 230 and 360 nm (Fig. 6.38). This is significantly different from the spectra obtained with the 3 M saturated air. Pure Pb has the highest absorbance (1.2-1.3 A) compared to the alloys (all around 0.9-1.0 A). The spectra after one week, compared to two weeks of exposure, are very similar. The spectra would indicate that pure Pb is most sensitive to acetic acid, both in the 0.3 M and in the 3 M AA saturated air. However, this is not supported by the gravimetric results, which show the largest increase in weight for the Pb-Sb alloys over pure Pb (Fig. 6.31).

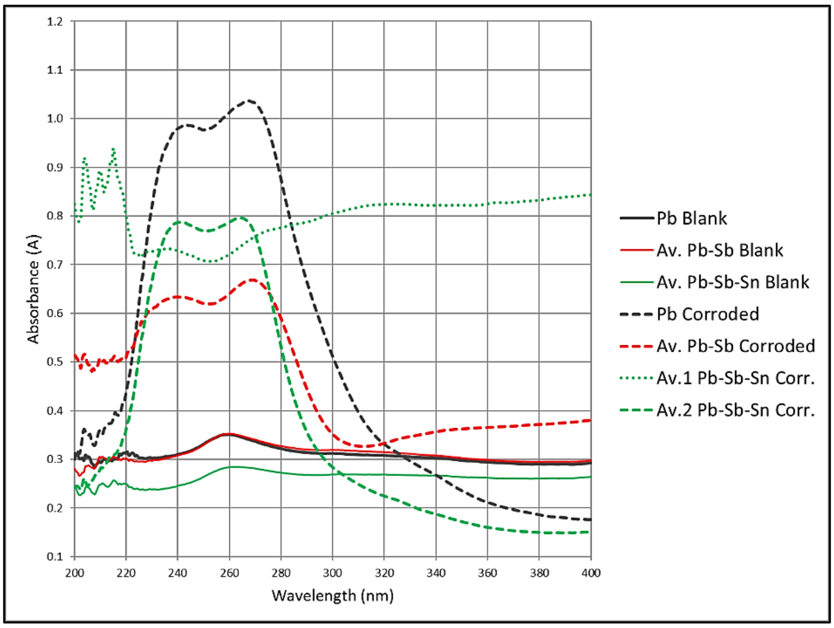


Fig. 6.37: Spectra of the uncorroded samples (full lines) and the corrosion layers formed in 3 M AA saturated air (dotted lines).

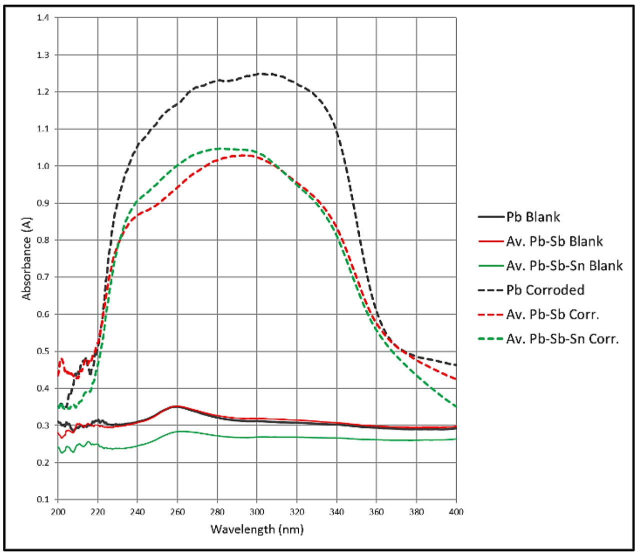


Fig. 6.38: Spectra on the corrosion from the 0.3 M AA saturated air, two weeks of exposure.

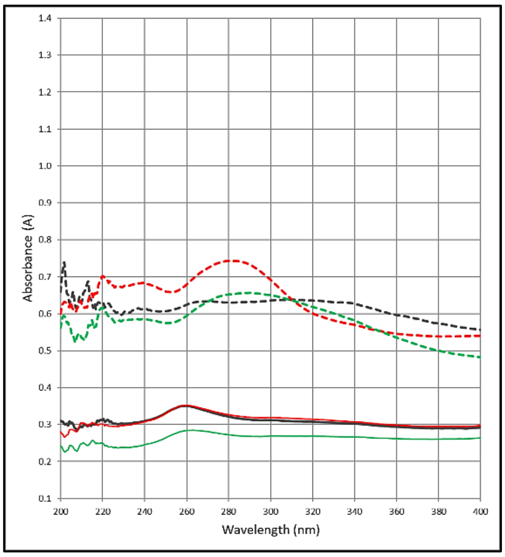


Fig. 6.39: Spectra of samples, exposed four weeks to the 0.03 M AA environment.

In contrast to the above results, the 0.03 M saturated air does show a rise in overall absorbance levels (from 0.5 to 0.7, Fig. 6.39) but did not result in distinctive curves or peaks after one week of exposure for any of the samples. After four weeks of exposure the spectra of the lead and the alloys showed a similar level of absorbance with values between 0.6-0.75 A, with a slight higher absorbance for the Pb-Sb alloys over the Pb and Pb-Sb-Sn alloys. Another observation is that with stronger solutions: the pure Pb generates a higher absorbance compared to the alloys. With less concentrated environments, this trend did not continue.

6.3.2.4 Formic acid environments

As explained in the chapter with the results from the acetic acid saturated air exposures, spectral results are grouped with an average for the Pb-Sb and the Pb-Sb-Sn alloys respectively, besides pure Pb. This chapter focusses on the comparison between the different concentrations of the formic acid atmospheres to which the samples were exposed. Also here, a selection of the most significant alloys is shown at microscopic level (Fig. 6.40), i.e. pure Pb, Pb-Sb 80-20, Pb-Sb-Sn 80-10-10 and Pb-Sb-Sn 80-8-12 wt%, exposed to a 0.3 M FA saturated air environment.

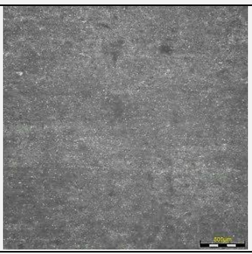
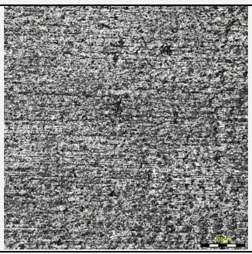
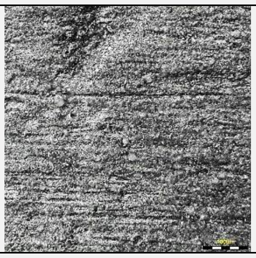
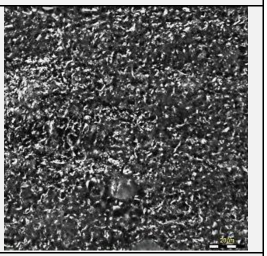
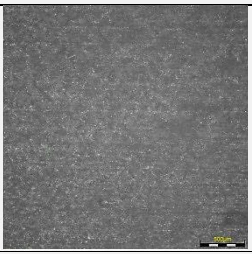
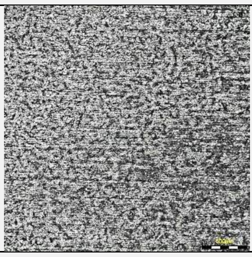
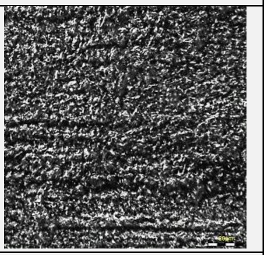
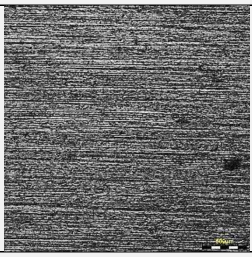
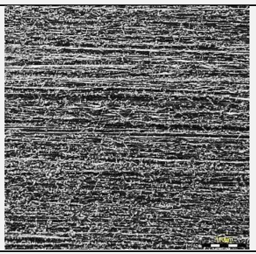
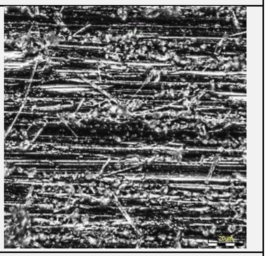
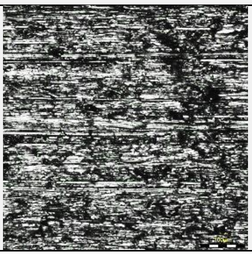
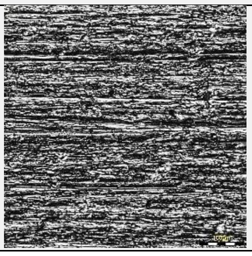
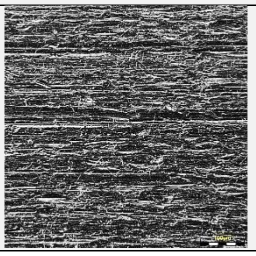
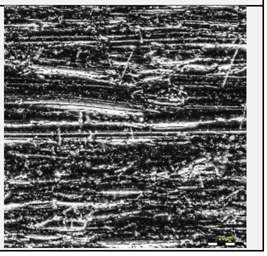
FA **0.3 M**	**100x BF** Scale bar 500 µm	**100x DF** Scale bar 500 µm	**500x DF** Scale bar 100 µm	**2000x DF** Scale bar 20 µm
Pure Pb				
Pb-Sb 80-20				
Pb-Sb-Sn 80-10-10				
Pb-Sb-Sn 80-8-12				

Fig. 6.40: Microscopic images from four lead and lead alloys, exposed to a 0.3 M FA environment.

The results from the samples exposed to the 3 M saturated air, show that the UV-spectra increase after one week of exposure for all alloys from an average of 0.3 to 0.6-1.0 (Fig. 6.41). Two distinctive peaks developed at 228 and 260 nm ±2 nm respectively. A noisy but significant signal is situated between 210-220 nm although the deuterium lamp spectrum has a relatively poor emission under 220 nm.

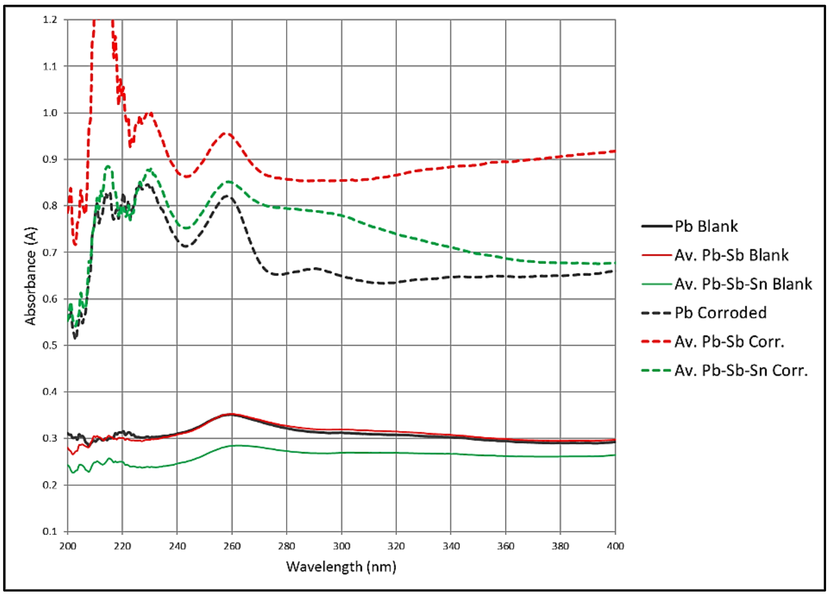


Fig. 6.41: Spectra from uncorroded samples (full lines); corroded samples after one week of exposure to a 3 M FA environment (dotted lines).

The samples from the 0.3 M saturated air shows identical peaks as with the 3 M solution, but without the high signal under 220 nm. The spectrum averages between 200-400 nm are clearly higher (0.5-0.9 A) than the non-corroded samples absorbance values (about 0.3 A), but are only slightly lower on the absorbance scale compared to the 3 M saturated air (Fig. 6.41). The highest values are recorded for the Pb-Sb alloys (0.7-0.9 A), intermediate values for pure Pb (0.6-0.75 A) and lower values for the Pb-Sb-Sn alloys (0.5-0.65 A). The differences between one week's and two weeks' exposure are only very small, smaller than 0.1 A for Pb as well as for the Pb-Sb or Pb-Sb-Sn alloys.

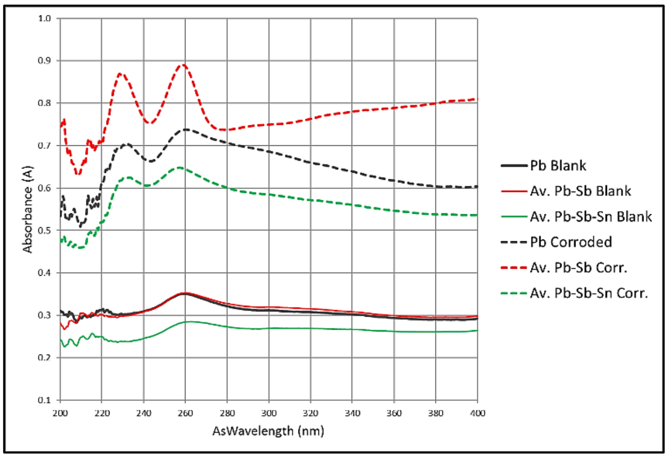


Fig. 6.42: Spectra on the corrosion from the 0.3 M FA envrionment after two weeks of exposure.

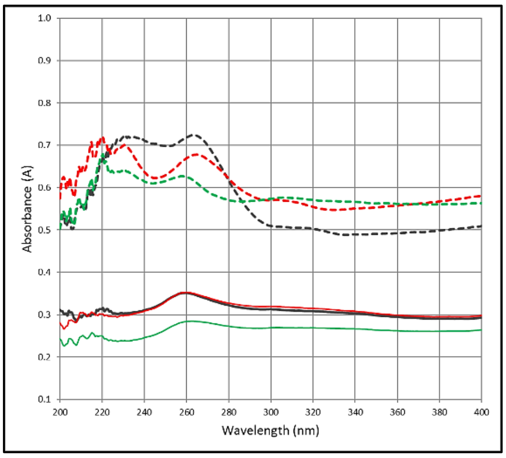


Fig. 6.43: Spectra from 0.03 M FA after four weeks of exposure.

The spectra on the samples from the 0.03 M FA environment show an increase in absorbance for all alloys from about 0.3 A to 0.5-0.7 A. Similar peaks to those from the more concentrated environments are determined, but were only defined after four weeks of exposure (Fig. 6.43). In more concentrated FA environments, the highest absorbance is generated by the Pb-Sb alloys and the lowest for pure Pb. Decreasing the FA concentrations of the formic acid, the absorbance values of Pb seem to increase compared to the alloys.

6.3.2.5 Comparison of UV-Vis reference spectra and corrosion products

In order to examine the possible relationship between the UV-Vis spectra and the identification of corrosion products, UV-range spectra of the main lead corrosion products related to this research (lead carbonate[2], lead acetate and lead formate) are presented in Fig. 6.44. Lead carbonate has a broad double peak at 240-255 nm and a shoulder in the region of 280-290 nm. Lead acetate has one relatively narrow peak at 250 nm and a steep drop towards 290 nm. Lead formate has a broad double peak at 240-260 nm with a high absorbance shoulder towards 310 nm. These features should enable identification of the respective corrosion products.

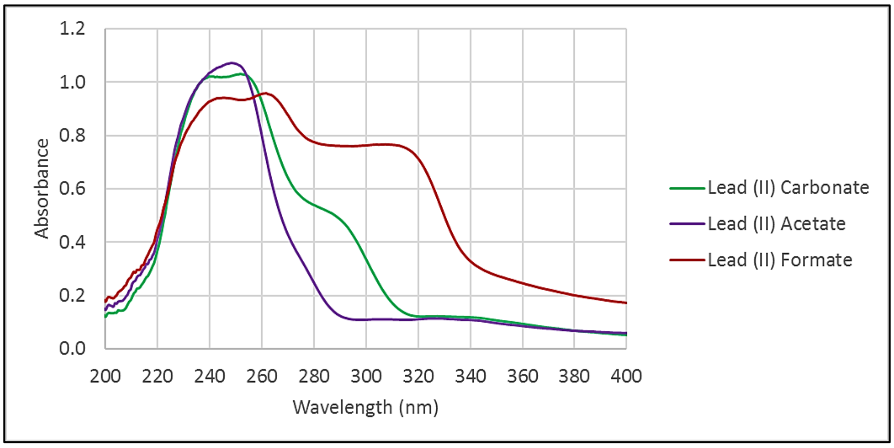


Fig. 6.44: Spectra of three lead corrosion products, white tile reference.

When comparing the measurements on the corroded samples (6.3.1) and the reference spectra, some observations can be made. With the samples exposed to air (6.3.1.1), the Pb-Sb alloys in particular show a significant rise in absorbance values (Fig. 6.45). However, no distinctive peaks are determined. The slight rise at 260 nm from the non-corroded lead (Pb blank) is sustained while there is a general increase in the absorbance values, most probably because of the lead oxidation.

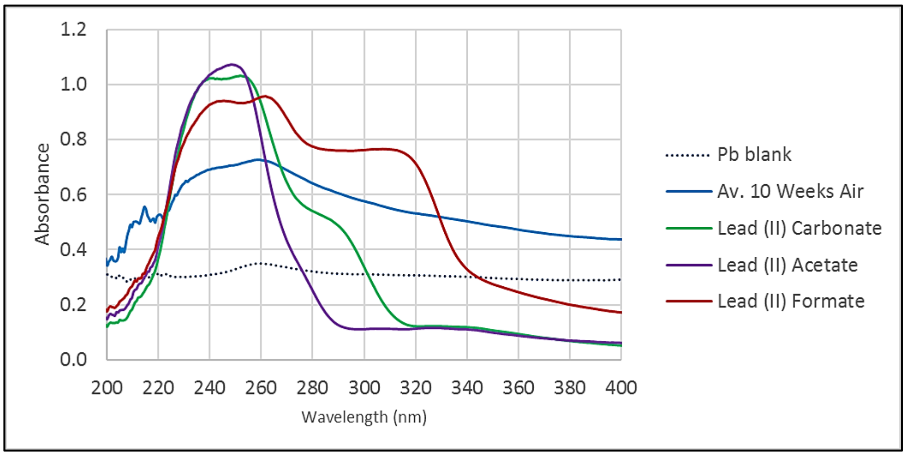


Fig. 6.45: Comparison of reference spectra and the average spectrum of the corroded Pb-Sb alloys from exposure to ambient air for 10 weeks.

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[2] The lead (II) carbonate used is a commercial available mixture of carbonates ($C_2H_2O_8Pb_3$), Acros Organics.

For the samples exposed to the 3 M acetic acid environment (6.3.1.2), a broad double peak was determined. The two peaks are formed at respectively 240 and approx. 265 nm (3 M AA Averages, Fig. 6.46). However, they do not correspond directly to the spectra of lead carbonates or lead acetates, two products that could be expected to have developed in the acetic acid environment.

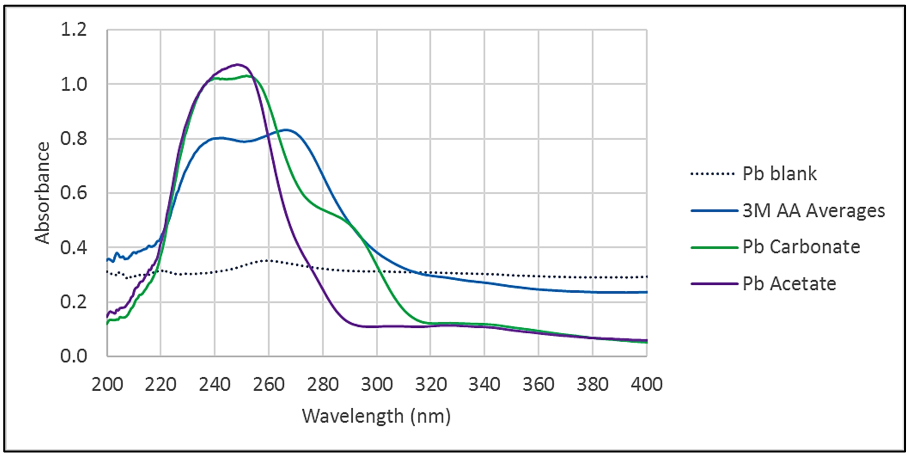


Fig. 6.46: Comparison of reference spectra and the average spectrum on the corroded lead alloys from the 3 M acetic acid saturated air.

The corroded samples from the 3 M formic acid environment (6.3.1.3) show in their averaged spectra two distinct peaks at 230 and about 255 nm, which are different wavelengths compared to the samples from the AA environment. Also, a shoulder in the spectrum of about 0.75 A is present, which resembles the spectrum of lead formate in the range of 280 until 310 nm (Fig. 6.47). Because of the grey appearance of the corroded samples as opposed to the white pure lead formate, the absorbance level towards 400 nm remains high at about 0.75 A.

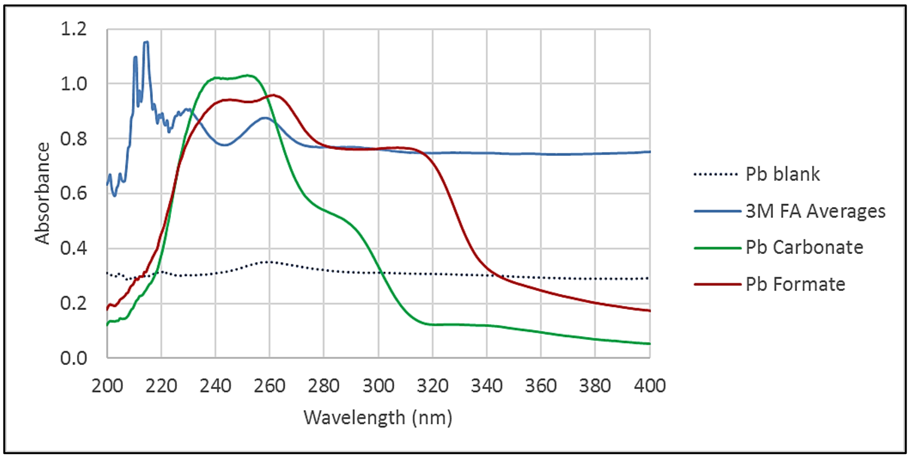


Fig. 6.47: Comparison of reference spectra and the average spectrum on the corroded lead alloys from the 3 M formic acid saturated air.

The spectra of the 3 groups of corrosion experiments do show differences, although no direct or clear relation to pure corrosion products can be made at this point. If the recording UV-spectra would be considered as a diagnostic tool for the determination of corrosion products, it is not clear at this point whether this is feasible or not. Further investigations are needed.

6.3.2.6 Discussion on the characterisation of corrosion products

For all alloys and all corrosive environments UV-Vis spectra show an increase in absorbance values with the development of corrosion products. This is especially the case in the UV-range between 200 and 400 nm, which also provides information independent of the actual colour changes of the sample. This was seen with the results from the strong acetic acid environment, where some samples developed a white product and were black, but generated similar peaks in the UV-range.

For the various corrosive environments, different peaks in the UV-spectrum were defined. The interpretation of these peaks in relation to the developed corrosion products is explored in 6.3.2.6. Corrosion development and the increase of the absorbance values are however difficult to define from the experiments. Although the strongest increase in absorbance is noted with the Pb-Sb alloys, which is in accordance with the CIE-L*a*b* results and the minor increased values for the Pb-Sb-Sn alloys that are less susceptible to corrosion, it was not possible to establish a direct relationship between the increase in absorbance values and the mass gain of the corrosion products. In order to do so, larger test pieces would have to be used to record sufficiently large changes in weight. Another way is to use electrolytic techniques, such as linear sweep or chronopotentiometric reduction of the corrosion products in relation to a defined surface area.

The identification of corrosion products by UV-Vis can be hampered by the broad peaks that are established – certainly compared to Raman or XRD for instance - or by other factors such as surface morphology or a combination of corrosion products that will cause overlaps. On the other hand, distinct spectra are to be obtained for specific corrosion products. This is shown in Fig. 6.48 where variations on lead carbonates are distinguished. As opposed to a more general lead carbonate product spectrum (Fig. 6.44), specific lead carbonates such as cerussite and hydrocerussite are identifiable. These products and their purity of mixture ratio were defined by µ-XRD. For each product, 3 spectra were collected and the averaged values are shown in the graph. More research however should be done to investigate the viability of this technique for the identification of corrosion products.

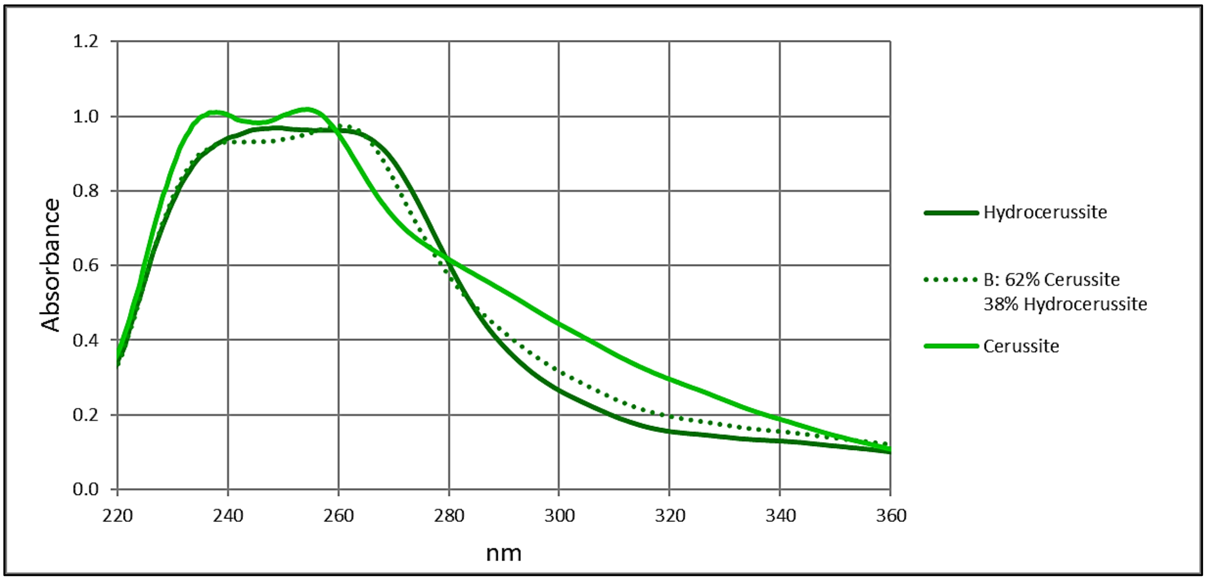


Fig. 6.48: Spectra of three differently composed lead carbonates, as identified by µ-XRD.

The possible added value with the UV-spectra can be found in the ease and speed of measurement, once this is developed to the next level. For this purpose, a large number of additional tests and comparisons with other analytical techniques have to be performed. Once spectra and specific peaks are identified for a range of corrosion products, evaluation of naturally corroded artefacts should be done to assess its capabilities with a view to future use in conservation.

It can be argued that many tools are already available (foremost µ-Raman, (µ-) XRD, FTIR or electrochemistry). However, as a quick and cheap evaluation method it could be used to assess metals as environmental sensors. In a number of situations, pollutant levels are very low and difficult or impossible to detect. A further advantage could lie in using a probe that is connected to the light source and a photo spectrometer, instead of using an integrated sphere. This would provide a contactless measuring method that leaves the sample or metal coupon untouched. The developed corrosion layer then stays undisturbed, which allows continuous or interval-based measuring during a certain period of corrosion development. Preliminary tests (not included in this paper) have shown to be promising.

6.3.3 Raman spectrometry on corroded lead alloys

6.3.3.1 Ambient air environment

The samples were exposed free lying in ambient air for a period of 10 weeks. The visual appearance of the samples is altered but shows no severe corrosion development (Fig. 6.4). Raman measurements were executed on Pb and Pb-Sb alloy with 16 wt% on two spots. Alloys also containing Sn were not measured because no corrosion product could be detected.

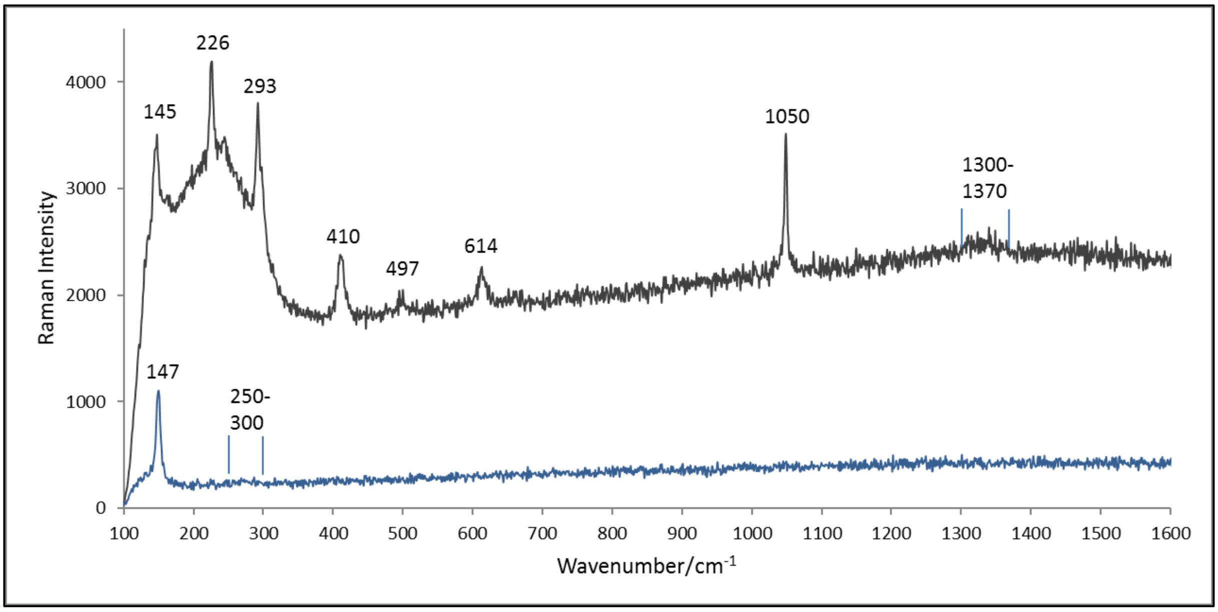


Fig. 6.49: Raman spectra of Pb (black) and Pb-Sb 84-16 wt% (blue) after exposure to ambient air.

Peaks on the Pb sample (black line in Fig. 6.49) are present on 145, 226, 293, 410, 497, 614, 1050 and around 1300-1370 cm^{-1}. Litharge (PbO) has reference peaks at 82, 147 and 339 cm^{-1}. Cerussite (ref. 225, 1052, 1370, 1477 cm^{-1}) and hydrocerussite (reference peaks at 421, 1052, 1371 cm^{-1} with a typical wide band peak between 1360-1380 cm^{-1}) could be present on these samples since the exposure took place in the laboratory where acids are also stored. When no corrosion product is detected, the Pb-Sb alloy (blue line) shows a peak at 147 cm^{-1} and a very wide but slight rise between 250-300 cm^{-1}, indicating metallic Sb, as the reference data (Ghiara, et al., 2014) for this element reports 114 (not visible in our spectra because of cut-off), 151 and 235-320 cm^{-1} respectively. Peaks at 293, 410, 497 and 614 cm^{-1} could not yet be identified.

6.3.3.2 Acetic acid environment

Measurements were executed on Pb, Pb-Sb alloys (16 and 20 wt%) and Pb-Sb-Sn (8 wt% Sn, 8 and 16 wt% Sb). Pb shows two different spectra: one spectrum (black line in Fig. 6.50) shows peaks at 151, 286, 340 (PbO?), 450, 475, 610-650, 915-930, 1052, 1350-1370, 1420-1480 and 2930. Cerussite (ref. 225, 1052, 1370, 1477 cm^{-1}) and lead acetate trihydrate (ref. from literature vibrational bands at 198, 466, 651, 815, 930, 1414, 1428 and 2926) seem to be present on both Pb and the alloys (Fig. 6.50-Fig. 6.52). The peaks at 286, 450, 475, 610, 915 and 1350 cm^{-1} could not be attributed.

The other spectrum (blue line) defines peaks at 143, 290, 392, 930, 1052, 1370 and 2930. The corresponding hydrocerussite references are 421, 1052, 1371 cm^{-1} with a typical wide band peak between 1360-1380 cm^{-1}. The peaks at 290 and 392 cm^{-1} could not be attributed.

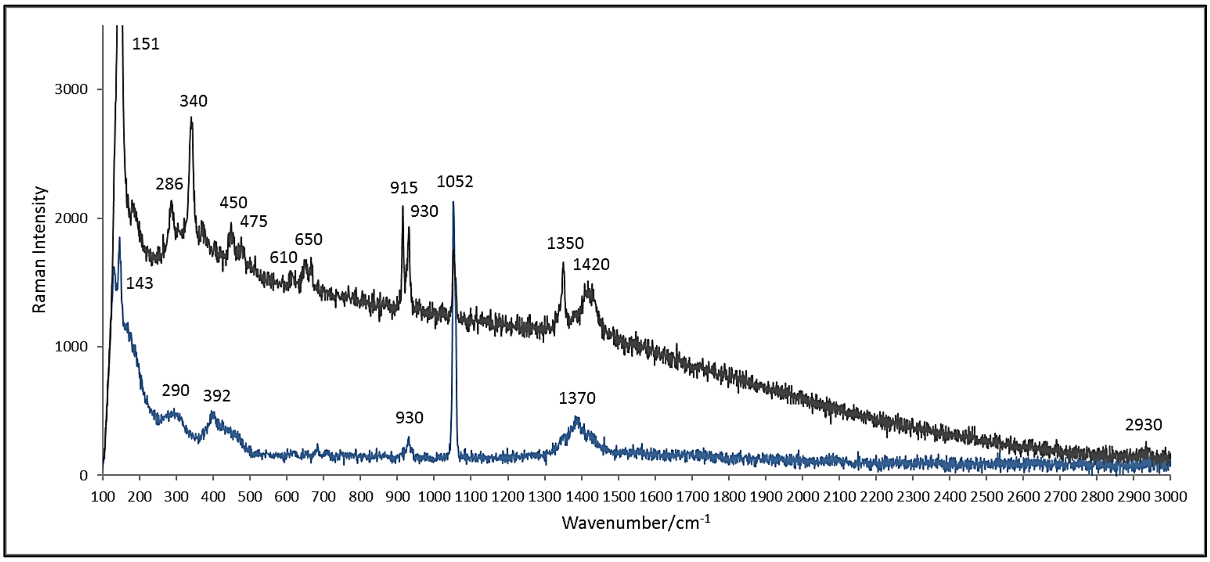


Fig. 6.50: Raman spectra on two different spots of pure Pb, exposed to an acetic acid atmosphere.

The Pb-Sb alloy 84-16 wt% shows two different spectra. One spectrum (black line in Fig. 6.51) shows peaks at 151, 266, 640-700, 930, 1052, 1370, 1390 and 2930. For metallic Sb, the reference data (Ghiara, et al., 2014) reports 114 (not visible because of cut-off), 151 and 235-320 cm^{-1} respectively. The second spectrum (blue) defines peaks at 151, 282, 400, 640-700, 930, 1052, 1370-1390 and 2930. This spectrum is very similar to the Pb spectrum in Fig. 6.50. The peaks of both spectra indicate similar corrosion products as in Fig. 6.50, blue line. Peaks at 282, 400, 640 and 1390 could not be attributed.

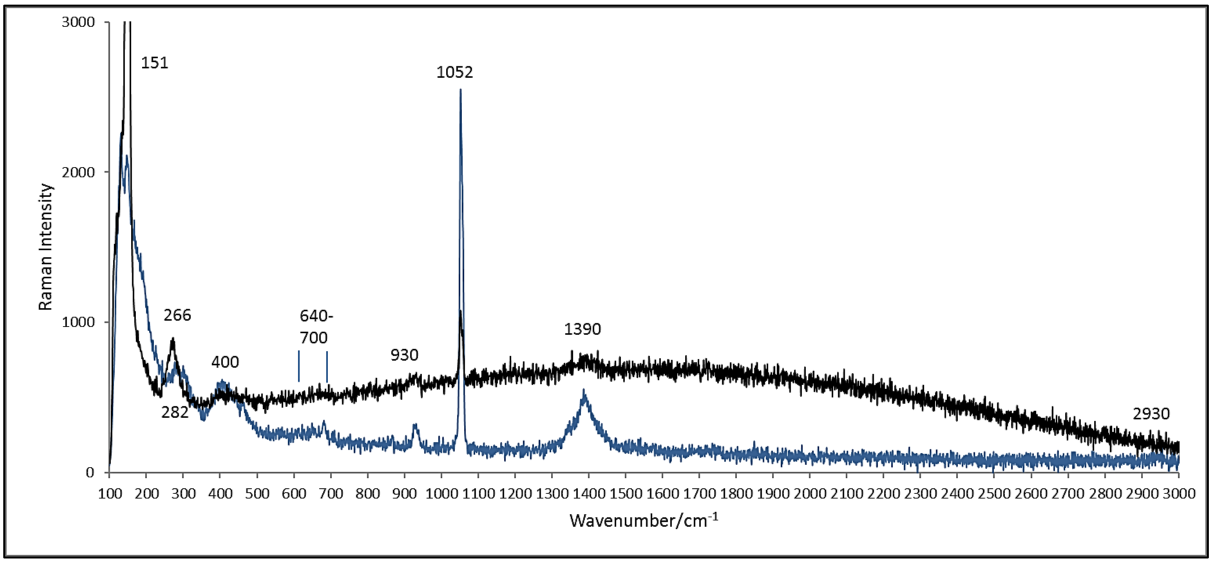


Fig. 6.51: Raman spectra on the alloy 84-16-00, exposed to an acetic acid atmosphere, measured at two different spots.

For the Pb-Sb-Sn alloys, spectra from two different alloys and three spots in total, show peaks (Fig. 6.52) at 151, 286, 370, 446, 477, 613, 650, 670, 916-930, 1051, 1350, 1414, 1540 and 2930. References for Tin (II) acetate show peaks at 209, 283, 335, 535, 670, 935 1343, 1425, 1560, 1642 and 2930 (Ghiara, et al., 2014). Peaks at 370, 446, 477, 613 and 916 could not be attributed. The three spectra show very similar results. A mixture of (hydro-) cerussite, lead acetate trihydrate and tin (II) acetate is very likely to be present.

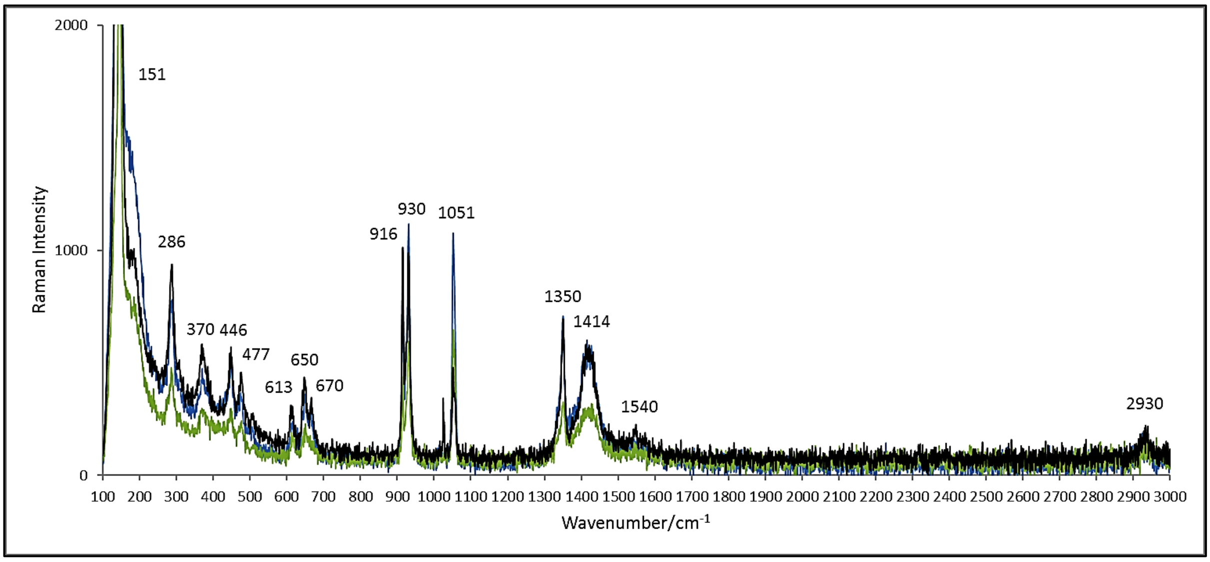


Fig. 6.52: Raman measurements on the Pb-Sb-Sn alloys 84-08-08 (two spots: blue and green line) and 76-16-08 (black line), after exposure to an acetic acid atmosphere.

6.3.3.3 Formic acid environment

Seven measurements were taken on three samples: two on Pb and five spots on Pb-Sb 84-16 wt% and 80-20 wt%. On two measured spots the Pb samples show different spectra, one without identifiable peaks (blue line in Fig. 6.53) and one (black line) with peaks at positions 150 (PbO?), 197, 758, around 1072, 1345, around 1535 and 1715 cm^{-1}. The most intense peak at 1345 cm^{-1} is related to Pb formate. Lead formate has reference peak positions on respectively 193, 757, 1065, 1343, 1374, 1531 and 2850 cm^{-1}. The unclear peak at 1715 cm^{-1} could not be attributed.

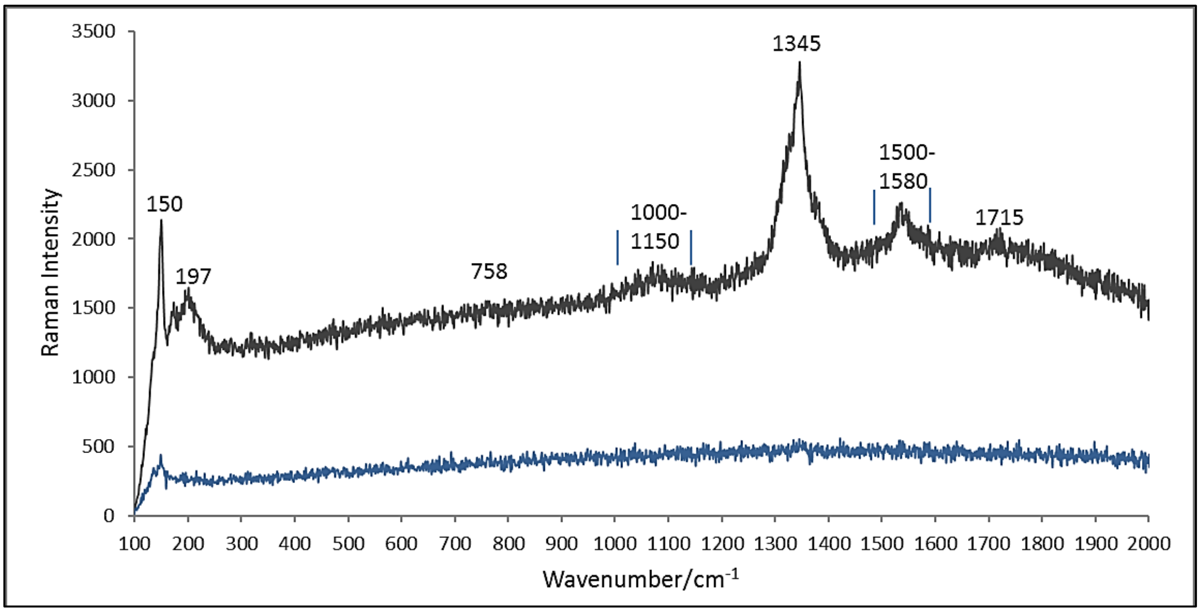


Fig. 6.53: Raman spectra from two spots on pure Pb exposed to a formic acid atmosphere.

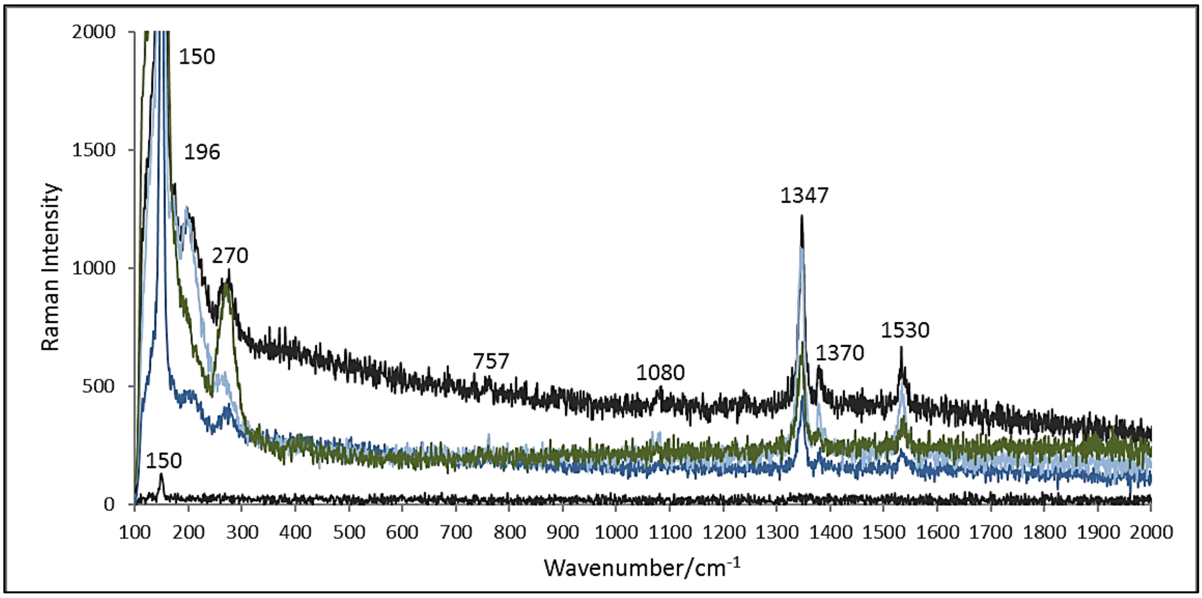


Fig. 6.54: Raman spectra from five spots on two Pb-Sb alloys exposed to a formic acid atmosphere, resp. 84-16 and 80-20 wt%.

For the Sb containing alloys, the main lead formate peaks at 196, 757, 1080, 1347, 1370 and 1530 are also shown, with additional peaks at 150 and 270 cm^{-1} indicating metallic Sb (Fig. 6.54). It is observed that the second peak of metallic Sb is much more pronounced when corrosion products are present, compared to a non-corroded sample (lower black line). This is most probably due to the fact that the non-corroded metallic Sb cubic crystals are present in the corrosion layer (Ghiara, et al., 2014) instead of being imbedded in the solid lead matrix, thus possibly gaining Raman intensity in the spectrum.

6.3.4 µ-XRD in reflectance on corroded lead alloys

On the selected lead and alloy samples as illustrated in Fig. 6.36 and Fig. 6.40, micro-XRD in reflectance (Reflection XRPD) was performed. The samples were respectively from the ambient air, acetic acid 0.3 M / 0.03 M and formic acid 0.3 M saturated air environments. A second set of samples from the acetic acid 0.3 M saturated air was measured as a double-check. The corrosion products that were identified, besides the metals, are listed in Table 6.1.

On the samples that were exposed to the ambient air atmosphere, only hydrocerussite could be measured on the pure Pb and the Pb-Sb 80-20 wt% alloy. The alloys with Sn did not provide any corrosion product identification.

The samples from the acetic acid atmosphere showed for Pb and the three alloys results for hydrocerussite, plumbonacrite and possibly lead acetate oxide hydrate.

The formic acid environment samples clearly showed lead formate as the only corrosion product present.

Table 6.1: Identified corrosion products with µ-XRD on lead and three selected alloys.

Composition Pb-Sb-Sn	**Ambient air**	**Acetic acid**	**Formic acid**
100 0 0	Hydrocerussite	Hydrocerussite Plumbonacrite Lead Acetate Oxide Hydrate (?)	Lead (II) formate
80 20 0	Hydrocerussite	Hydrocerussite Plumbonacrite Lead antimony oxide (?) Lead Acetate Oxide Hydrate (?)	Lead (II) formate
80 10 10	-	Hydrocerussite Plumbonacrite Lead Acetate Oxide Hydrate (?)	Lead (II) formate
80 8 12	-	Hydrocerussite Plumbonacrite Lead Acetate Oxide Hydrate (?)	Lead (II) formate

6.4 Discussion

The reactivity to corrosive environments was measured for binary Pb-Sb alloys compared to pure Pb and to the ternary Pb-Sb-Sn alloys. The results for the binary Pb-Sb alloys have shown that a stronger corrosion development was present in all environments, straight from the minimum concentration of 4 wt% Sb up to 20 wt%. This complies with other findings (Storme, Jacobs, & Lieten, 2013) (Ghiara, et al., 2014). The presence of the antimony-rich crystals provokes the corrosion reaction of the adjacent lead. Electrolytic measurements (OCP*) have shown a more positive potential for Sb (-0.60 V/MSE*) compared to Pb (-0.93 V/MSE) and Sn (-0.97 V/MSE) in acidic solutions. This galvanic corrosion results in a fierce protrusion of corrosion products, breaking up the antimony crystals (Fig. 6.55, top left image: cross section before corrosion) and giving a crater-like structure at the surface (bottom left image and 3 D-image on the right, results after exposure to a formic acid atmosphere).

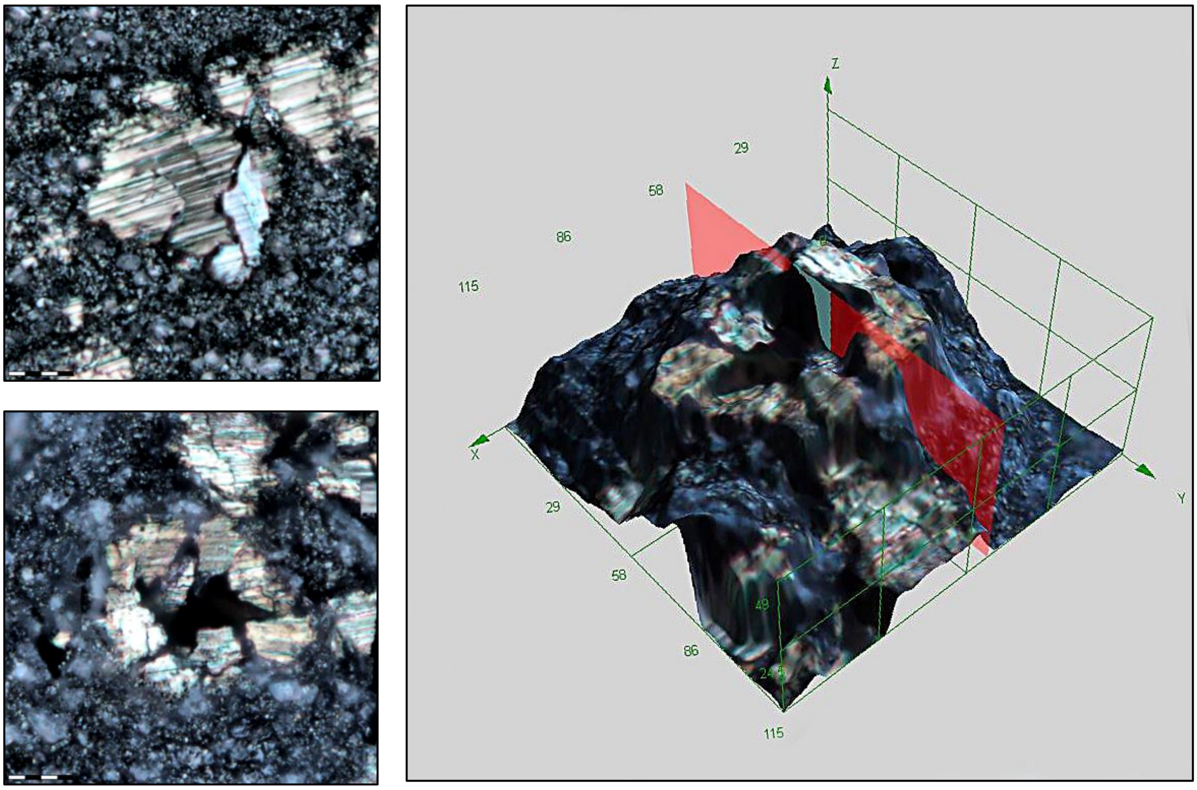
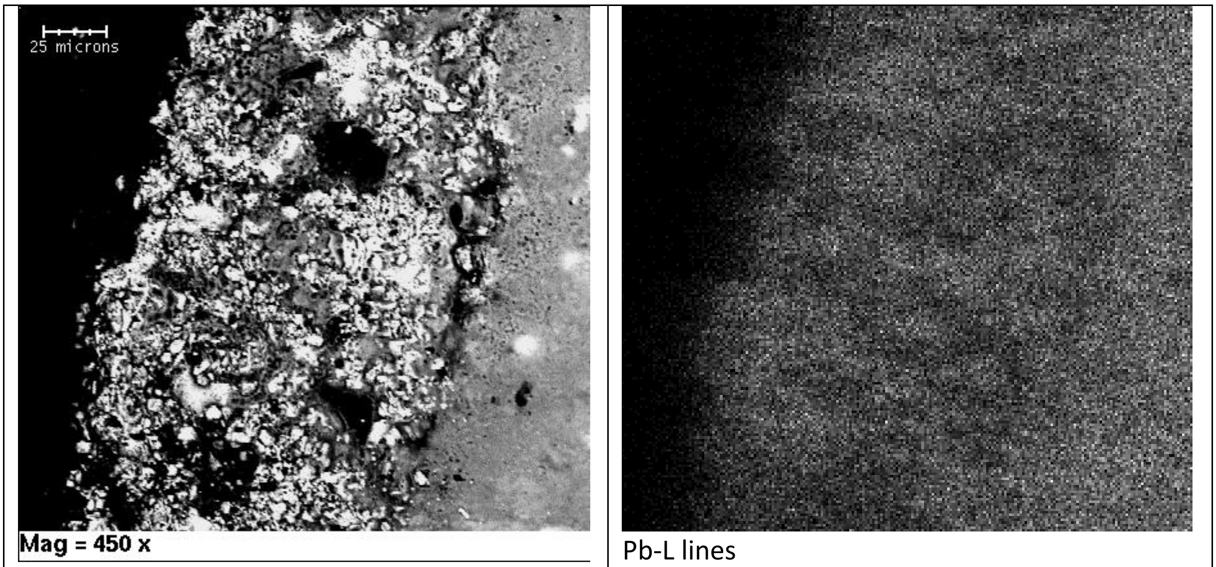


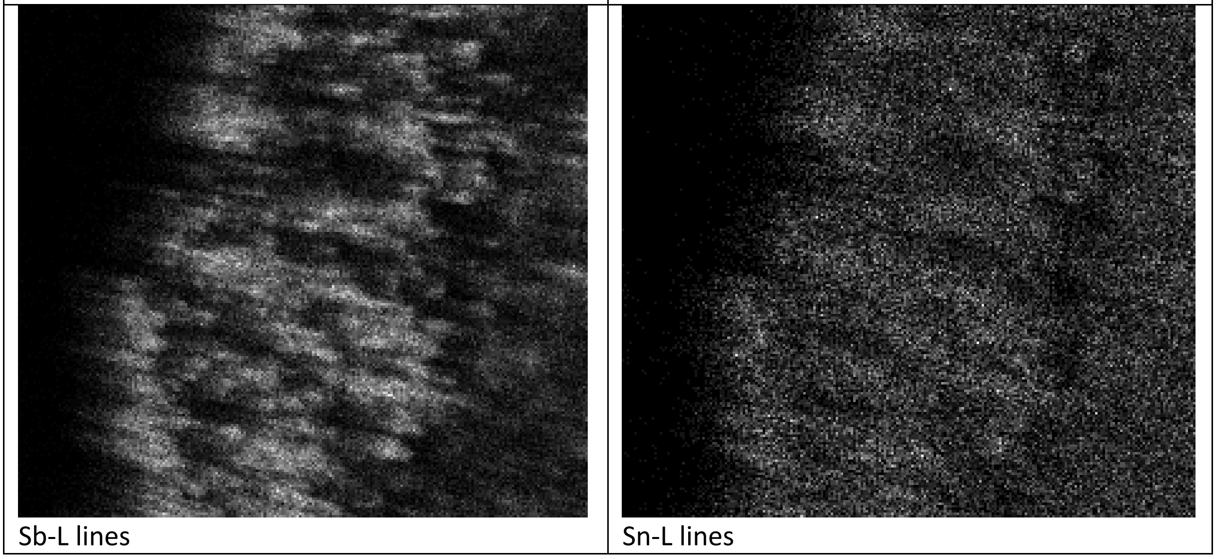
Fig. 6.55: Microscopic images at 2400x magnification with a DSX500 microscope in Brightfield modus, of a cubic antimony crystal in a lead rich matrix before corrosion (top left) and after exposure to a formic acid atmosphere (bottom left and right 3 D-image).

It is known that elements with limited or no solubility in the lead rich matrix, such as Cu or Sb, precipitate at the grain boundaries and might promote localised corrosion (Degrigny & Le Gall, 1999). It is also suggested that the formation of columnar grains favours the progress of fissure into the bulk, which could be responsible for the large expansion corrosion (Costa, 2005) (Cattaneo, Stumph, Tillmann, & Sassmannshausen, 1997). Another reason can be the formation of micro-porosity in the casted type, as reported with casted grids for batteries (Simon, 1968).

Similar corrosion development has been observed on historical types. An example is given in Fig. 6.56 with severe corrosion development on a type piece R 136-o. The corrosion layer has strongly expanded and carries Sb crystals in its volume. This is illustrated by the light areas in the bottom left image, showing the occurrence and distribution of the antimony crystals. The Pb is evenly distributed in the alloy bulk and in the corrosion layer (top right). The Sn is probably linked to the Sb content (bottom right), with the formation of a pseudo-eutectic alloy in the lead rich alloy matrix. This is also shown in the SEM-EDX results on the microstructures in chapter 4 (4.3.1.5).



Pb-L lines



Sb-L lines

Sn-L lines

Fig. 6.56: SEM-EDX mapping of a printing type with severe corrosion development. Top left: backscattered image of the metal core and corrosion layer; top right Pb distribution; bottom left Sb distribution; bottom right Sn distribution.

The ternary Pb-Sb-Sn alloys as composed in this study, do not show this specific corrosion formation. As described in literature, Sn inhibits the corrosion of lead. In these alloys, also the formation of SbSn crystals play a role, diminishing the potential difference compared to the lead. The SEM-EDX measurements on the Sb-rich phases (chapter 4) have shown ratios of about 50:35 wt% Sb:Sn. Further investigations on these phenomena could be carried out using extended SEM-EDX and micro-electrochemical measurements.

Coming back to the very high reactivity of the binary lead-antimony alloys to corrosive environments, they could serve as highly sensitive metal sensors. The results in this chapter have shown that surface changes were already measurable after one week. Their reactivity is linear with the antimony concentration. At 12 wt% antimony, a eutectic alloy is established while at higher concentrations (e.g. 16 or 20 wt%), antimony crystals segregate from the lead matrix.

Metal sensors are usually used as a set of three, being a silver, a copper and a lead coupon to determine different compounds from the atmosphere that corrode the respective sensors. Subsequently, visual and/or electrochemical techniques are often applied to determine the corrosion products (Costa & Dubus, 2007). In the case of lead, a wide range of atmospheric pollutants may react with its surface, producing corrosion products such as oxides, sulphides, sulphates, acetates, formates, chlorides, nitrates or different kinds of carbonates. Nonetheless antimony is present in the Pb-Sb sensor alloy, mainly Pb-corrosion products are generated since antimony rarely corrodes. In the performed tests in this study, no antimony corrosion products could be measured from the tested environments.

An additional advantage of using Pb-Sb alloys is their higher hardness compared to pure lead. This enables an easier preparation of the metal sensors, because they are far easier to polish to a predefined grade (e.g. P 2500). The combination of fast corroding sensors and an easy evaluation system could give way to the simultaneous use of multiple sensors throughout a building for the localisation of VOC sources.

The colour measurements on the one hand and the UV-range spectrophotometric results on the other indicate that for all lead alloys, but especially for binary Pb-Sb alloys, corrosion monitoring is possible over much shorter time periods compared to traditional pure lead metal sensors. The use of UV-Vis for the measurement of chemical changes at a surface could enable the easy and fast interpretation of the environment corrosiveness, although many analytical techniques already exist to define corrosion products (e.g. Raman, XRD or FTIR). The results of the µ-XRD and the Raman-measurements in this study are clear and in accordance with each other, however Raman seems to present a few products which were not detected with µ-XRD in reflectance. These are litharge and cerussite on the air-oxidised samples and tin (II) acetate on the Pb-Sb-Sn samples from the acetic acid atmosphere. In case of the cerussite on the oxidised samples, a reason could be found in the (partial) transformation of hydrocerussite into cerussite over time.

Further research towards the identification of corrosion products using UV-spectrophotometry has to be done. It is important to distinguish protective layers from ongoing corrosion formation to establish a reliable measuring system for conservation purposes.

6.5 Conclusions

Binary lead type alloys with antimony show the strongest corrosion development in all tested environments. Ternary lead type alloys, including antimony and tin are less affected, because of the inhibiting effect of the tin. These alloys show CIE-L*a*b* results that are often in the range of pure Pb corrosion development, meaning that the addition of tin only roughly balances for the antimony content. In acetic acid environments, the addition of tin inhibits the lead corrosion better compared to formic acid environments, where the effect is less pronounced.

The corrosion products that developed in the atmospheric tests depend firstly on the atmosphere to which samples were exposed. For Pb and Pb-Sb alloys only Pb corrosion products such as oxides, carbonates and formates were measured. No antimony corrosion products were detected. For the ternary alloys, and only in the acetic acid atmosphere, additionally Sn acetates were measured.

Lead-antimony alloys may be used as superfast sensors, combined with a surface evaluation using UV-Vis spectrophotometry. As an alloy, lead-antimony offers a higher reactivity to environmental substances compared to pure lead. Two additional advantages are present, as antimony only provokes the lead corrosion without forming antimony corrosion products at the one hand and the fact that lead-antimony alloys have a much higher hardness compared to pure lead, thus enabling easier polishing of the surface prior to the atmospheric exposure.

UV-Vis measurements and more specifically UV-spectrophotometry suggests to be an alternative evaluation method for the corrosion development on objects and on lead coupons as monitoring sensors. A range of corrosion products produces very specific spectra in the UV-range (220-400 nm). There is a rapid response on first oxidation, even when the corrosion product is not yet developed to a sufficient layer, needed for identification by other methods (e.g. Raman or XRD). UV-range spectrophotometric measurements may also be executed in an continuous mode. Disadvantages of the method are to be expected with combined corrosion products that will give overlapping spectra or dark corrosion products (e.g. oxides, sulphides) that give no distinct peaks in the UV-spectra.

6.6 Conservation directives

6.6.1 Monitoring the museum environment

In the Museum Plantin-Moretus, as in most museums, temperature and relative humidity (RH) are controlled at certain locations in the exhibition and storage rooms. Because of the wide range of materials present in the museum, it is virtually impossible to indicate one ideal level for temperature or RH. Therefore, average values are chosen and kept stable as well as possible. However, even though temperature and RH are important factors in the development of corrosion, the foremost causal connections between corrosion effects are to be found in environmental parameters, more specifically harmful pollutant concentrations. These pollutants, namely volatile organic components (VOC's, i.e. acidic gasses), can be present in high but also in very low concentrations, and are therefore difficult or impossible to measure on a continuous and widespread basis throughout the museum.

Metal coupon sensors, combined with temperature and relative humidity measurements, are recommended for continuous use. In this way, long-term evolutions and fluctuations can be registered. Former research projects have shown that the abundant presence of oak in the museum is not favourable for lead corrosion. It is however impossible to replace all oak items with inert materials. Therefore, a constant monitoring and realistic mitigation actions should be applied to minimise the VOC's present in the museum atmosphere. The airflow in the museum rooms is important since acidic gas concentrations can be avoided by a continuous through-flow of fresh filtered air. An investigation will be carried out on the feasibility of this measure, given that a series of doors to the outside are opened by visitors, as they follow the recommended sequence of exhibition rooms.

6.6.2 Monitoring the lead type collection

Preventive conservation methods and actions emerge for monitoring and maintaining the museum environment in the best possible conditions with regard to lead corrosion. For the lead types on display, whether in the trays or as standing type in the showcases, it is advised to inspect them visually on a scheduled basis (e.g. twice a year).

For the types that are kept in trays with a closed hardboard lid, it is strongly recommended to change the lid to an inert and transparent material (e.g. polycarbonate). This prevents the additional emission of VOC's from the hardboard but also enables visual inspection without the need to open the lids. Another feature that could be added to the transparent lids is the introduction of a gap between the tray and the lid, preventing an accumulation of acid gas concentrations in the tray compartments with the types. To avoid dust coming in, a filter lining can be introduced in the gap.

Finally, for the lead types that are kept in paper wrapped packages, XRF measurements can be done through the paper to select the lead-antimony sets from those that also contain tin. Subsequently, a number of each group could be opened up for inspection concerning possible corrosion development. Depending on these results, action can be undertaken as discussed in the following parts.

6.6.3 Treatments for the lead types

Conservation treatments for lead objects can be divided into non-corroded and corroded objects. Non-corroded objects could be treated by cleaning superficial dust or other layers at the surface. Subsequently, a chemical stabilisation and/or a protective layer could be applied to protect the lead alloys from their environment, thus preventing corrosion. However, it has been shown that none of the present available and acknowledged conservation techniques are sufficient to prevent corrosion when VOC's are present (Speerstra Joel, 2011). Therefore, the removal of endangered types from harsh environments and placing them in a space with clean air, low humidity and a stable temperature will always be a preferable preventive solution.

Corroded objects can be treated, but their original surface or in some cases their original metallic structure cannot be regained. There are many possible methods, such as mechanical cleaning with the use of scalpels, glass fibres, pencils, etc. These techniques are often used in combination with chemical cleaning techniques. It should however be remembered that lead corrosion products are often harder than the underlying lead or alloy, endangering the information that lies beneath the corrosion layer.

In this respect, chemical treatments that focus on the removal of the corrosion layer without, or with a minimal intervention on the original bulk material, should be considered. In the past, acids have been frequently used to clean lead objects from corrosion, but lately EDTA or one of its salts is used in weak acid solutions from lead complexes and prevents the formation of non-soluble lead hydroxides (Costa, 2005). The use of ammonium acetate is recommended to remove all corrosion products if the conservation choice supports this.

More recent conservation evolutions have led to laser and plasma cleaning. However, plasma cleaning, whether in a low pressure plasma or with an atmospheric plasma torch at very low temperature, is not capable of removing the often thick corrosion layers on lead objects. Laser cleaning was used successfully in a few cases, but is not applicable for the vast number of lead types present in the MPM collection.

Electrolytic treatments are regarded as the least invasive techniques on lead objects when applied appropriately (Degrigny & Le Gall, 1999). The main goal with these treatments is to establish corrosion reduction by providing the object with electrons by means of galvano- or potentiostatic devices (Carradice & Campbell, 1994). This is possible by emerging the object in a bath (the electrolyte) or working locally with a so-called electrolytic pencil. The use of an electrolyte over a chemically active solution (e.g. acid solutions) is preferred because a well-chosen electrolyte does not attack the metal core of the object and simply serves as a circuit for transporting ions. Solutions with sodium carbonate or sodium sulphates are amongst the safest options for electrolytic treatments (Costa, 2005).

Besides the reduction of corrosion layers, it is also possible to perform so-called 'consolidative reduction', meaning that the corrosion products are not only reduced to metallic lead, but the latter would also stay in place and regain the original mass of the object. However, this is not easy to implement in practice for a number of reasons. First, corrosion products grow and expand on the surface, using metal from the bulk and thereby displacing atoms. Secondly, the reduced lead is not then structurally attached to the metallic bulk as it was before, resulting in a loose layer that cannot be maintained without additional consolidation (Costa, 2005).

Finally, a post treatment is always rendered mandatory to decrease the chemical reactivity of the cleaned surface. If not, certainly in non-ideal atmospheric conditions, new corrosion will start up again very fast. One of the techniques tested was to rinse the lead objects in dilute sulphuric acid to establish a formation of a sulphate film, in order to determine the lead's reaction to other chemicals. It was shown however that this kind of treatment does not develop a film that really protects against harsh environments. At its best, it can slow down oxidation in relatively clean atmospheric conditions. Other passivation techniques such as anodic polarisation to develop oxidations films in sulphate or potassium iodide solutions were also tried (Costa, 2005). The latest developments for protecting lead surfaces include the use of carbonyl mono-layers, to produce an inhibiting film (De Keersmaecker, De Wael, & Adriaens, 2012) (De Wael, et al., 2010) (Dhooghe, 2006). Although CIE-L*a*b* experiments are promising, there is no certainty that these kinds of treatment will work on historical objects with variated alloys or surface conditions, or if they could withstand manipulation and long-term exposure to non-ideal atmospheric conditions. For the cleaning and preservation of organ pipes, rinsing in water was also suggested as an easy technique in order to dissolve the water-soluble compounds on corroded surfaces, resulting in a more stable object surface. CIE-L*a*b* results have however shown that no advantageous effects are achieved by doing this (Speerstra Joel, 2011). A last step in trying to protect the cleaned surface is the application of a wax of lacquer as a sealant for the environment. Within the group of waxes, the microcrystalline kinds have more beneficial properties than animal or vegetable waxes, e.g. they are more water-repellent and can be obtained in a range of melting temperatures (e.g. MCW Amber) (Speerstra Joel, 2011). This range includes soft and adhesive kinds up to hard and firm hardening coatings. In the case of lacquers, Paraloid® B72 is often used in conservation for the protection of all kinds of objects, including lead. There are however controversial results on the protectiveness obtained in test conditions (Speerstra Joel, 2011). It should be borne in mind that the layer applied has to completely cover the objects and be even in thickness in order to obtain a good level of protection. Every manipulation can cause damage to the often soft or brittle layer, resulting in accelerated corrosion development at the damaged zone. This indicates that protective layers should only be considered when minimal or no manipulation, mounting or movement of the items is expected.

It is beyond the scope of this study to go further into the technical aspects of different treatments for lead objects and more in particular the lead type at the MPM. However, if conservation treatment were required for heavily corroded objects, this is something that has to be addressed in its own right. The key issue in treatment choice lies in the decision about whether an object is kept for its artefact value and material information or whether it has to be treated to save the legibility of the surface, in this case for instance the type's face. Regarding the lead types which are severely corroded in the MPM collection, this kind of decision is comparable to archaeological artefacts. The overall goal is always the concern for conservation, namely selecting the appropriate treatment, materials and environment for storage and exhibition (Costa, 2005). However, as stated above, none of the current available and ethically approved conservation techniques can guarantee that an object will stay free of corrosion forever, certainly not when the atmospheric conditions cannot be maintained at optimal levels (Costa, 2005). Therefore, it might be advisable to use more permanent consolidation techniques if a certain face on types is to be safeguarded for the future.

6.6.4 Selection, exhibition and storage facilities

A selection of those lead types that are at greater risk of corrosion, i.e. the lead-antimony alloys without tin, should be safeguarded. It is recommended to select them from the collection by means of visual inspection for current corrosion issues and to use XRF measurements to separate the types with or without tin from each other. Since the types without tin mainly seem to originate solely from the 18th and 19th century, they are not of a major importance for the public exhibition. Yet for the collection itself and for research, they might be highly significant, since for a number of them no matrices are kept in the museum and these types are the sole survivors for certain faces.

This should however not draw attention away from the other types. As the experiments have shown, lead-antimony alloys containing tin have a comparable corrosion reactivity to pure lead. Therefore these types should also not be regarded as completely safe from corrosion, and the guidelines for keeping the museum as free from VOC's as possible should be established as far as possible.

As the recent study of the atmospheric conditions at the MPM has shown (Krupińska, van Grieken, & De Wael, 2013) there are considerable levels of VOC's present, in particular acetic and formic acids. Additional metal sensor measurements (Storme, Jacobs, & Lieten, 2013) have shown that in showcases, the levels of VOC's can even be higher than in the museum rooms. This is due to the closed micro-environment and the wood of the showcases that emits harmful gasses to the inside, where they accumulate. For this particular problem, the aeration of the existing showcases (e.g. opening them every week) could be a low-tech solution to minimise the pollutants effects. Another option could be to introduce vapour phase corrosion inhibitors (VPIs) inside the showcases to absorb the VOC's (Speerstra Joel, 2011). A more sustainable solution would be to alter or change the showcases with inert materials, but this might be a problem since the styles of the showcases are often complementary to the museum interior.

On the subject of storage facilities, the recent adaptations of the museum with a new library, conditioned storage facilities (primarily for books and documents) and a full reorganisation have allowed for the installation of appropriate technical equipment in the historic house on the Vrijdagmarkt. The storage of metals (lead types, copper matrices and copper engraving plates) depends on a stable temperature and RH as low as possible. In addition to these requirements, clean air (i.e. free of VOC's) is the next most important safeguard. This can be established by installing an air conditioning system with filters at the air vents. The most efficient means of filtering VOC's from the ambient air is active carbon filter systems (Cruz, Pires, Carvalho, & de Carvalho, 2008). It goes without saying that no new VOC-emitting materials should be introduced into the storage rooms. Cabinets, shelfs or racks should be made with absolute zero emitting materials such as metals, glass, stone or plastics (e.g. polyethylene, polypropylene, polycarbonate, polymethyl-methacrylate). Assembling or painting should also be done without emitting VOC's known to be released from certain acrylic kits or a variation of paints. Materials without these specifications should be tested first on their emission properties. Finally, continuous monitoring of the air (temperature, RH and VOC's) remains mandatory to keep the metal collection in optimal condition.

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7 Conclusions

Content

7.1 Conclusions on the lead type

7.1.1 Type alloys, composition and microstructure

The production of a set of reference lead-antimony-tin alloys offered the possibility to investigate their microstructure, distribution of elements, physical properties and chemical reactivity in corrosive environments. The composition is decisive for the hardness of the alloy, one of the most important factors for the handpress bookprinters. Since the establishment of the printing system with lead types, there was a constant search to find the highest hardness accompanied by a sharp cast in the matrix, at the lowest material cost possible. The results do indeed show that the addition of mainly antimony, but also tin, increased the hardness of the casted letter. However, the variation in hardness is not huge within the investigated group of alloys, representative for historical alloys: HV 20 ±5 compared to about HV 4 for pure lead. This might explain why it was not mandatory for the letter casters to adhere strictly to a predefined alloy composition, but rather to be allowed some freedom in casting. The wide variation in the measured compositions may represent and confirm this.

The phases in the microstructure of the alloys vary greatly and are also dependent on the cooling rate of the cast. From this, small type are to be considered undercooled alloys with a higher dissolution of elements (as antimony) in the lead rich phases than the phase diagram indicates for room temperature solid solutions.

The investigation also showed that reference alloys for lead-antimony-tin alloys are mandatory for checking the numeric results from software used with analytical equipment, such as XRF or SEM-EDX instruments. Since these alloys are seldom used in industry today, software algorithms often seem to be incorrectly calibrated.

7.1.2 Historical type alloy compositions

X-Ray Fluorescence analysis proved to be useful for determining concentrations of antimony and tin in the lead type alloys. When measuring a wide range of lead type in the Plantin-Moretus collection, presumed to be from the 16th century, it appeared that there was a very large variation in alloy compositions, even within founts. The facts that the workmen at the time did not have analytical instruments, that they recycled large amounts of material, and that they could change an alloy composition on the spot when casting was problematic, led inevitably to the use of this wide range of alloys. The results show that the 16th century types contain more tin, whilst more recent casting (i.e. 18th century) only contains antimony and no tin. This was primarily for economic reasons as tin was very expensive at that time, but also because the production of antimony had become cheaper and easier. The quality of the casted type could be maintained, even when no tin was added. In modern times, tin was added again for even better quality castings, certainly when (semi-) automatic casting machines were used from the late 19th century onwards.

The measurement results for the 16th century types correspond to the relatively small number of former measurements, but are able to demonstrate vast differences in alloys between sets of types, even within founts themselves. It shows that a large number of measurements are needed to obtain an objective view of the compositions used for a certain fount. Comparison of the analytical results also indicate whether certain parts of a fount belong together or not. It seems that in more recent times, from the 18th century onwards, the composition of the casted items is more homogeneous. This is no surprise, since quality control and refining techniques allowing the use of more purified metals had been improved over the centuries.

7.1.3 Corrosion

The tests with corrosive environments have shown that binary lead alloys containing only antimony are much more prone to corrosion development than pure lead. The antimony has a promoting effect on the development of lead corrosion products. The ternary lead-antimony alloys that also contain tin show a lower level of corrosion reactivity than the binary alloys. In acidic environments, the concentration of tin should be higher than the concentration of antimony to establish the inhibiting effect, compared to pure lead. More specifically, the results suggest that a maximum antimony concentration of 8 wt% combined with 8 or 12 wt% tin is less reactive than pure lead. Higher concentrations of antimony and/or lower tin content result in more corrosion development in the conditions that were investigated. It has to be stressed that no alloy can be regarded as completely inert to acidic atmospheres. In all cases, but especially for the lead-antimony alloys, extreme care has to be taken in the protection, exhibition and storage of the historical types. The analytical results on 16th century types show that the ratio antimony/tin is mostly favourable for preservation. Results on 19th century lead types, however, indicate high antimony levels, which means they are at great risk of corrosion development.

At the same time, the fast corrosion rate of lead-antimony alloys opens up a possibility for the development of new environmental measuring metal sensors to detect volatile organic compounds in the atmosphere, together with a fast method for evaluating corrosion development, as shown with UV-Vis measurements. Measurements in the visible light region (CIE-Lab results) as well as in the UV-range (absorbance values increase and peak formation) could open up new opportunities for controlling spaces at multiple points, at short time intervals and with a fast and cheap evaluation method. However, the precise methodology and comparative measurements for establishing corrosion rates and corrosion product identification are to be examined further.

7.2 Conclusions on the copper matrices

7.2.1 XRF measurements on the copper matrices

The collection of matrices at the Museum Plantin-Moretus is world famous for its magnitude and its significance. From a material point of view, it is remarkable that so many traceable ‘pure’ copper pieces are kept within one collection. Since it is to be expected that copper from the 16th to the 18th centuries would not be completely free of other elements in its composition, possible information from the compositional variations was examined. An analytical approach using X-Ray Fluorescence apparatus was implemented at the museum site. The apparatus and its results provide information about the copper composition of the matrices. This information can be used to complement historical facts and earlier research.

7.2.2 Statistical approach to the analytical results

The results on about 9000 individual matrices were investigated for the possible relationship between alloy composition, attributed punchcutter and his probable location and time of work. Because of the complexity of the data, it is difficult to discover relationships between the copper alloy compositions on the one hand and historical facts on the other. Pairwise comparison of alloys according to the most prominent elements present (i.e. lead-antimony or zinc-tin) gave useful but limited information on the match between matrices. However, when all measured elements in the copper alloys (8 metals) were taken into account simultaneously, this method was no longer valid.

Statistical grouping was therefore considered a useful tool for the evaluation of multiple measurement results. The results revealed that groups of alloys were constructed by the program algorithms and that these groups could be connected to known historical facts. First, matrices already attributed with a high certainty were described. Secondly, matrices that were not clearly documented were investigated to match. Matrices where there was doubt or no knowledge at all about attribution were directed to a certain group, leaving information for further investigation. Even though the method proved to be valid in most cases, the mathematical calculation results have to be monitored against the average values of each group. It was noted that in some cases a group of alloys (i.e. a set of matrices) was dedicated to a certain group on the basis of their non-fit rather than on the basis of a true fit in the particular group.

7.2.3 Relationship to historical facts

The present study of matrices and their composition is a first attempt in this field. Therefore, only preliminary ideas can be put forward and more research is needed to establish a wider reference grid. In spite of this, information on three levels has already been obtained: 1. The control of the homogeneity of individual matrix composition within a certain set; 2. Possible uniformity in alloy compositions between sets of matrices, attributed to a certain punchcutter; and 3. Compositional differences between sets of matrices from punchcutters, in location and over time.

The first results indicate groups of alloys that can be connected to certain punchcutters such as Van den Keere, Granjon or Le Bé. A part within these results is particular because a number of matrices are made in brass, the majority in the Plantin-Moretus collection most likely produced by Granjon while he was working in Lyon. Other groups show different compositions for coppers used in Flanders, Paris or Lyon in the 16th century. Other groups show divergent results for 16th century vs. 18th century copper compositions based on the arsenic content. It must nevertheless be stressed that this study is a first attempt to correlate alloy compositions with punchcutters-matrix makers, their active period and working location. Further research is definitely required to build a wider reference grid and increase the amount of statistical data in order to confirm the results presented in this study. In addition, more measurements on matrices from the Museum Plantin-Moretus, but also from other collections, would be highly beneficial in constructing an extensive data set. Finally, these analytical results should not be seen in isolation. They should be related to other facts from archival documents and to complementary research that is performed on punchcutters and their work.

7.3 Final conclusion

The world-famous typographical collection at the Museum Plantin-Moretus has been studied thoroughly for many decades and much information has already been gathered and published. However, an analytical approach to the materials present in this collection, more specifically the lead type alloys on a wide scale and uniquely the copper matrices, has never been attempted until now. These copper matrices are unique in their concept and existence. The punchcutters at the time ordered the 'most pure copper' available on the market, in order to strike their valuable punches without the risk of breaking them. In this respect, we witness the materials that were believed to be the purest copper from a certain time and location. Furthermore, each of these copper pieces are uniquely marked because of the particular typeface they bear. The results presented here establish that there is more information available from the material characteristics. Analytical measurements combined with statistical grouping prove to be an additional and complementary tool for researchers examining historical typographic material. These findings may lead to an even better understanding of the history of handpress printing in its wider sense. Moreover, this study may reveal an undiscovered iceberg of information, of which barely the tip has been exposed.

The results on the corrosion of lead types are of direct use for conservation purposes. They confirm that lead-antimony alloys are much more sensitive to acidic environments, developing severe corrosion and possible total loss of items. The addition of tin to the alloy inhibits the corrosive reactions to some extent. The advice to the museum is on the one hand to provide sufficient ventilation to prevent the accumulation of acidic atmospheres, while on the other to screen the lead collection for their specific alloy compositions. This will allow for a selection of items that are most susceptible to corrosion and their removal from the permanent collection into appropriate storage conditions. Lead types with a sufficiently high tin content can be left in the exhibition cabinets for visitors to view. These actions ensure the function and character of the Museum Plantin-Moretus while safeguarding the lead type collection for future generations.

8 Samenvatting

Historische koper- en loodlegeringen in het museum Plantin-Moretus, Antwerpen.

Inleiding

Het museum Plantin-Moretus te Antwerpen is erkend als werelderfgoed door de UNESCO, omwille van haar uitzonderlijke geschiedenis, bibliotheek, archief, gebouwen en objecten maar bovenal voor de rol die de drukkerij in de gouden jaren van Antwerpen heeft vervuld. Vele studies en publicaties werden reeds hieraan gewijd, steunende op de geschreven stukken die zich in het museum bevinden. Een onderzoek naar de materiële informatie dat zich in de typografische objecten zou kunnen bevinden, werd echter nog nooit systematisch toegepast. Deze insteek vormt dan ook de grondslag voor dit onderzoek, waar twee onderzoeksvragen naar voren worden geschoven:

1/ In hoeverre kan analytisch onderzoek op de materialen bijdragen tot een betere conservering van de objecten in het museum; en
2/ In hoeverre kan materiaalinformatie bijdragen aan het historisch onderzoek.

In de eerste plaats zijn wij schatplichtig aan Plantin en zijn opvolgers, niet alleen voor datgene dat zij gepresteerd hebben maar bovenal omwille van het nauwgezet bijhouden van archiefstukken en het bewaren van het typografisch materiaal. Deze zaken waren cruciaal om de voorliggende studie uit te voeren, meer bepaald het onderzoek op de loden drukletters en de koperen matrijzen.

Literatuuronderzoek

Vanuit de historische literatuur werden de werkmethodes en materiaalsamenstellingen van enerzijds loden drukletters en anderzijds koperen matrijzen beschreven. De voornaamste bronnen hiervoor waren Biringuccio (De la pirotechnia, 1540), Moxon (Mechanick Exercises, 1683) en Fournier (Manuel Typographique, 1764). De belangrijkste stappen in het proces van het handmatig drukken vanaf de late 15de eeuw bestond er in om stalen stempels voor elk van de tekens van het alfabet te snijden, deze vervolgens af te slaan in koperen staafjes zodat er matrijzen verkregen werden, om tenslotte de loden drukletters in de matrijzen af te gieten. Het ontwerpen en vervaardigen van de stalen stempels werd gedaan door zgn. ‘stempelsnijders’ zoals Garamond, Granjon, Le Bé, en anderen. Tot aan het eind van de 16de eeuw zorgden zij er ook voor dat de stempels werden afgeslagen in het koper om aldus de matrijzen te verkrijgen. In eerste instantie werden sets van matrijzen doorheen heel Europa verkocht, totdat steeds vaker ook de stempels werden verkocht. Op deze manier kon elkeen die de stempels bezat, zoveel matrijzen slaan als hij wilde, op voorwaarde dat de stempels niet braken. Het gieten van drukletters werd door drukkers meestal uitbesteed aan gieters, die zich specialiseerden in het op maat maken van de matrijzen (het zgn. ‘justeren’) voor een bepaalde druk. Vervolgens goten zij het aantal letters dat de drukker nodig had om een reeks boeken te maken. De belangrijkste 16de eeuwse lettersnijders en lettergieters van wie er nog origineel materiaal in de collectie van het museum Plantin-Moretus aanwezig is, zijn Garamond, Granjon, Le Bé, Haultin, Guyot, Sabon en Van den Keere.

Onderzoek naar loodlegeringen, zoals deze voor drukletters werden gebruikt

Om onderzoek uit te voeren op de loden drukletters, enerzijds om metingen te doen naar hun samenstelling en anderzijds op hun corrosiegevoeligheid, werd een set van historisch relevante legeringen aangemaakt. Deze legeringen bestaan uit lood met antimoon of uit lood, antimoon en tin.

Er werden in totaal 15 loodlegeringen aangemaakt met variaties van 0-20 % antimoon en van 4-12 % tin, in stappen van 4 %. De aangemaakte legeringen werden geverifieerd op hun samenstelling. Vervolgens werd deze set gebruikt om het in dit onderzoek gebruikte XRF-toestel (X-stralen Fluorescentie) te kalibreren en zo het meten op loodlegeringen toe te passen. De resultaten tonen aan dat het gebruikte toestel (een Olympus-InnovX Delta Professional) met de bijhorende software betrouwbare resultaten geeft voor het meten van de loodlegeringssamenstellingen. De aangemaakte loodlegeringen werden daarnaast ook op enerzijds hun microstructuur onderzocht en anderzijds op hun hardheid.

Het kennen van de microstructuren is relevant voor het begrijpen van corrosieve reacties. De conclusies van dit onderzoekdeel zijn overeenkomstig met de literatuur, namelijk dat bij lood-antimoonlegeringen hoger dan 12 % antimoon er zich afzonderlijke antimoonkristallen afscheiden in de loodrijke matrix. Bij de legeringen waar ook tin aanwezig is, zien we het ontstaan van mengkristallen van tin en antimoon, in het bijzonder bij de legeringen met een hoger antimoongehalte dan 12 % en met meer dan 8 % tin.

De hardheid meten van de verschillende legeringen is relevant om een objectief overzicht te krijgen van de variaties in hardheid en hun relatie tot de praktijk van het drukken, waarbij de stelling is dat letters in hardere loodlegeringen langer meegingen alvorens zij vervangen dienden te worden. Toevoeging van 5 tot 16 % antimoon in het lood zorgt voor ongeveer een vier maal hogere hardheid ten opzichte van lood. Het bijkomend toevoegen van tin zorgt voor een vijf- tot zesvoudige verhoging van de hardheid en biedt bovendien een dunnere vloeibaarheid van het gesmolten metaal, wat tot fijnere afgegoten letters leidde. Het besluit over de hardheidswaarden van de verschillende legeringen is dat het niet bijzonder veel uitmaakte welke verhouding de loodlegering precies had, omdat de verschillen in hardheden niet erg groot waren. Het was belangrijker om tegen een hoog tempo kwaliteitsvolle fijn gegoten letters te produceren en daarbij kwam de ervaring en het inzicht van de lettergieter op de eerste plaats. Als resultaat van de metingen op historische letters zien we dan ook een zeer brede waaier van lood-samenstellingen omdat de gieters destijds enerzijds geen analytische middelen hadden om de legeringen die ze gebruikten precies te kennen en anderzijds omdat men de samenstelling van het gesmolten metaal aanpaste tijdens het gieten zelf totdat zij snel en efficiënt goede letters verkregen.

Onderzoek naar de samenstelling van de koperen matrijzen

Uit de collectie matrijzen van het museum, zo'n 20.500 in totaal, werden bijna 9000 stuks individueel gemeten met XRF om hun kopersamenstelling te kennen. Deze analyses werden gekoppeld aan de vermeende makers van de matrijzen, de periode waarin zij werden vervaardigd en de vermoedelijke plaats waar de maker werkzaam was. Deze gegevens werden op twee manieren verwerkt. Een eerste methode was om de belangrijkste elementen (naast het koper zelf) te beschouwen. In de koperen matrijzen bleek dit vooral lood en antimoon te zijn. In sommige matrijzen werd ook arsenicum aangetroffen en een deel van de matrijzen was niet in koper gemaakt, maar in messing door de toevoeging van zink. Door de elementen grafisch voor te stellen en de gegevens te koppelen aan bekende sets, was het mogelijk om tendensen te zien in het soort koper dat bijvoorbeeld Van den Keere in Gent gebruikte tegenover het koper dat Le Bé in Parijs gebruikte om zijn matrijzen te slaan.

De tweede methode was een statistische verwerking met alle gemeten elementen naast het koper. Deze waren in eerste instantie lood, antimoon, zink en arsenicum, maar ook tin, ijzer, zilver en nikkel werden als waarden in deze verwerking meegenomen. Het resultaat was een optimale groepering van tien legeringsvarianten, waarbij de variatie in elke groep zo klein mogelijk werd gehouden ten opzichte van een zo groot mogelijk verschil tussen elk van de groepen, clusters genoemd. De methode bleek nuttig te zijn om met grote datasets om te gaan en tendensen van elkaar te onderscheiden. Het bleek echter ook nodig om elke matrijs of matrijzenset apart te controleren aan de hand van de aanwezige elementen en de eventueel beschikbare historische informatie. De beide methoden worden dan ook als complementair aan elkaar beschouwd.

De voornaamste clusters die samengesteld konden worden, zijn de volgende:
Cluster 1: Koper met lood en antimoon, maar ook met arsenicum, exclusief toegewezen aan Hendrik van den Keere.
Cluster 2 en 4 zijn gelijkaardige kopersoorten met lood, met zeer weinig of geen antimoon. De stempelsnijders die hieraan gekoppeld kunnen worden zijn Le Bé, Haultin en Granjon, werkzaam in Parijs of Lyon.
Cluster 3 en 5 zijn eveneens gelijkaardig in hun kopersamenstelling en blijken het sterkst overeen te komen met Van den Keere in Gent en Granjon terwijl hij in Antwerpen werkte.
Cluster 7 is deze waar zink het belangrijkste element is en daarmee de messing matrijzen aangeeft. De grootste groep van de gemeten messing matrijzen kan worden toegewezen aan Granjon, vanuit zijn vroege periode wanneer hij nog in Lyon werkte.
Cluster 9 is een kopersoort waar ook arsenicum in gevonden werd, maar in een hogere concentratie vergeleken met cluster 1. Deze groep kan exclusief worden toegewezen aan 18de eeuwse stempelsnijders-matrijzenmakers zoals Rosart, Smit en Van Wolsschaten.
Cluster 10 bestaat uit 1 matrijzenset, MA 9, dewelke als enige in lood is vervaardigd.
Clusters 6 en 8 behelzen een relatief klein aantal matrijzen en hun samenstellingen lopen nogal uiteen. Deze clusters blijken op zich niet bijzonder waardevol om toewijzingen te doen, het lijkt er eerder op dat het statistisch algoritme deze matrijzen uit andere clusters heeft weggehouden dan ze werkelijk als groep zijn samengezet.

Onderzoek naar corrosie-ontwikkeling bij loodlegeringen

De set loodlegeringen, aangemaakt zoals boven beschreven, werd gebruikt om de corrosie-ontwikkeling in verschillende atmosferen te onderzoeken. Naast een proef aan de lucht werden verder voornamelijk azijnzuur- en mierenzuur-omgevingen met verschillende concentraties gecreëerd in luchtdicht afgesloten desiccatoren. De loodlegeringen die hierin corrosie hadden ontwikkeld, werden vervolgens gemeten op hun kleurverandering, op hun corrosieproduct-samenstelling met Raman en X-stralen Diffractie en tenslotte met UV-spectrofotometrie in reflectie.

De kleurveranderingen, volgens het CIE-L*a*b*-kleurenmeetsysteem, tonen aan dat de legeringen die uit lood met antimoon gelegeerd het sterkst corroderen. De verschillen in waarden tussen het onaangetaste oppervlak en na de corrosie-ontwikkeling, zijn duidelijk sterker verschillend ten opzichte van de legeringen waar ook tin werd aan toegevoegd. Op basis van deze waarnemingen kunnen we stellen dat de aanwezigheid van het tin daadwerkelijk de corrosie vermindert in gelijke omstandigheden.

De samenstelling van de corrosieproducten is logischerwijs direct gekoppeld aan de omgeving waaraan zij werden blootgesteld. De loodlegeringen die aan de lucht werden geoxideerd, hadden wel een kleine kleurverandering, maar ontwikkelden te weinig corrosieproduct om met Raman of XRD te worden gemeten. De loodlegeringen die aan azijnzuur-omgevingen werden blootgesteld ontwikkelden vooral loodcarbonaten en loodacetaat, terwijl daarnaast de legeringen die ook tin bevatten, eveneens tinacetaat ontwikkelden. De legeringen die aan de mierenzuur-omgeving werden onderworpen, ontwikkelden voornamelijk loodformiaat.

De UV-spectrofotometrische metingen in het spectrale gebied van 220-400 nm tonen dat er voor elk van de legeringen, ook deze aan de lucht blootgesteld, een snelle stijging is van de absorptiewaarden ten opzichte van niet-gecorrodeerde equivalenten. De verschillende ontwikkelde corrosieproducten tonen elk bovendien een verschillend spectrum, waarmee in theorie de soort corrosie zou kunnen geïdentificeerd worden. Deze spectra komen echter niet geheel overeen met metingen op zuivere loodzouten zoals loodacetaat, loodcarbonaat of loodformiaat. Een reden hiervoor kan gevonden worden in mengsels van corrosieproducten die zijn ontstaan op het oppervlak of doordat de structuur van het oppervlak de oorzaak is van de afwijkingen in het spectrum. Desalniettemin is het feit dat er met de relatief eenvoudige meting in het UV-gebied een snelle respons waarneembaar is bij elke vorm van oxidatie op het oppervlak van de loodlegeringen. Dit zou bijvoorbeeld kunnen ingezet worden bij het bewaken van de luchtkwaliteit in musea.

Richtlijnen voor conservatie en bewaring

De authentieke inrichting van het museum Plantin-Moretus met zijn eikenhouten vloeren, balken, meubels en letterkasten, is bijzonder om te bewaren maar vormt tegelijk een ongunstige atmosfeer voor de bewaring van de loden drukletters. Eikenhout genereert immers organische dampen, die het lood aantasten. Metingen in het recente verleden hebben aangetoond dat er inderdaad azijnzuur en mierenzuur-dampen aanwezig zijn in het museum, met een duidelijk hogere concentratie ten opzichte van de waarden buiten het museum. Tezamen met de waarnemingen dat vooral de loodlegeringen met antimoon, zonder tin, het sterkst corroderen in zure omgevingen, zijn de richtlijnen voor het museum duidelijk: Het is noodzakelijk om de collectie op hun samenstellingen te screenen om vervolgens in eerste instantie de loodlegeringen die geen tin bevatten, onder te brengen in een meer geschikte, zuurvrije omgeving. Voor de bewaring van de overige drukletters, die een integraal deel uitmaken van de tentoonstelling in het museum, wordt aangeraden om zoveel mogelijk ventilatie en/of luchtzuivering te voorzien zodat de zuurwaarden in de lucht zo laag mogelijk blijven. Om corrosie van metalen tegen te gaan is een zeer lage relatieve luchtvochtigheid gunstig, maar dit is onmogelijk te bereiken in het museum omdat alle andere houten interieurdelen, meubels en schilderijen hieronder te sterk zouden lijden.

Besluit

Betreffende de onderzoeksvraag naar het beter begrijpen van corrosieprocessen op de specifieke loodlegeringen bij historische drukletters en het beter kunnen bewaren van deze collectie, heeft het onderzoek aangetoond dat de loden drukletters gevaar lopen om gecorrodeerd te worden in de zure omgevingslucht van het museum. Zeker de legeringen met antimoon en zonder tin in hun samenstelling zijn hieraan bijzonder gevoelig.

De metingen op loodlegeringen die aan verschillende zure omgevingen werden blootgesteld, geven aan dat UV-spectrofotometrie beloftevol is om op een snelle manier met relatief eenvoudige middelen oxidatieprocessen op metalen aan te tonen. Dit kan nuttig zijn voor het bewaken van de luchtkwaliteit in het museum Plantin-Moretus en andere.

Tenslotte hebben de analytische metingen op de koperen matrijzen relaties blootgelegd tussen de samenstelling van het koper van de matrijzen en hun makers, periode en plaats. Deze methode kan derhalve in de toekomst worden ingezet om twijfelachtige toewijzingen of onbekende matrijzensets alsnog te kunnen identificeren en zo het historisch onderzoek te ondersteunen.

Attachments

Content

1 Abbreviations

A: Absorbance value
Acc: accents (letters)
Ag: Silver
As: Arsenic
BF: Bright Field, direct light to the observation geometry in optical microscopy
Bi: Bismuth
Caps: Capital (letters)
CTS: Centro Tecnologico Sperimentale S.R.L., laboratory in Ceparana, Italy
Cu: Copper
DF: Dark Field, indirect light to the observation geometry in optical microscopy
Fe: Iron
Hg: Mercury
HV: Hardness Vickers
ICP-OES: Inductive Coupled Plasma with Optical Emission Spectroscopy
K: Kelvin (degrees)
keV: Kilo Electron Volt
KIK-IRPA: Koninklijk Instituut voor het Kunstpatrimonium – Institut Royal pour la Patrimoine d’Art
lc: lower case (letters)
lig: ligatures (letters)
MPM: Museum Plantin-Moretus
MSE: Mercury/mercury Sulphate Electrode
Ni: Nickel
nm: nanometer
nos: numbers
OCP: Open Current Potential
OM: Optical Microscopy
ppb: parts per billion
ppm/ppmv: parts per million (volume)
punct: punctuations (letters)
Raman: Analytical technique
Sb: Antimony
SEM-EDX: Scanning Electron Microscope with an Energy Dispersive X-Ray Detector
Sn: Tin
UA: University of Antwerp
UV-Vis: Ultra Violet and Visible light spectroscopy
VOCs: Volatile Organic Compounds
Vol%: volume percent
wt%: weight percent
XRD: X-Ray Diffraction, analytical technique for crystallography by using X-rays
XRF: X-Ray Fluorescence, analytical technique for measuring elements with X-rays
Zn: Zinc
µg: micro gram

2 Glossary

Acicular: needle-shaped

Alloy: composition of two or more metals

Anneal (to-), Annealing: heating a metal or alloy to a point of recrystallization, which softens the metal or alloy after cooling down

Anvil: iron or steel block on which hammering or striking of another object is performed

Bearing(s): metal parts in a machine that support axles to rotate with minimal friction

Binary alloys: composed of two metals

Brass: alloy of copper and zinc

Break-off: removing the upper piece (the tang) from the body of freshly cast type

Bronze: alloy of copper and tin, often 5 to 20 wt% Sn, sometimes with additions of other metals

Cast (to-), Casting: Melting of metal and pouring it into a mould to solidify in a certain shape

Comet tails: traces in the polished surface of a sample due to a small hard particle in a softer matrix

Cupellation: purifying silver by adding lead to the melt, which binds impurities in a porous crucible

Die (-piece): Hard metal piece with a certain shape or design used to stamp a softer metal to the corresponding negative shape or design (e.g. stamping of coins with a die and counter-die)

Dressing: making fresh cast type to a predefined height to fit the printing instruments

Electrotyping: galvanic method to reproduce items in a mould using the deposition of dissolved metals in an electrolyte (electric conductive liquid solution)

Eutectic: solid solution of two metals in a certain ratio, resulting in a fine and equally distributed microstructure

Forge (to-), Forging: plastic deformation of a metal by hammering (room temperature or heated)

Fount: a complete set of types for printing

Grain: cluster of metal atoms within a polycrystalline microstructure of a solid metal or alloy

Ingot: hollow shape in heat-resistant material to cast molten metal into, where it solidifies

Justify (to-), Justifying, Justification, Justifier: filing down of a strike to make it fit a mould (instrument), thus making it a matrix

Lye: strong alkaline solution (e.g. sodium hydroxide)

Matrix, Matrices: Justified strike that fits in a mould (instrument) to produce types

Matrix (in a solid alloy): Bulk composition of the alloy, in which different phases may be present

Mould (to-): making a negative form to cast liquid metal into, solidifying in the mould producing the negative shape

Oddy test: procedure to evaluate the (corrosive) influence of certain products (i.e. liquid solutions, solid materials off-gassing, etc.) by using air tight containers, which hold a metal specimen, the product to be controlled for its corrosive vapours and a small amount of water. In the recipient, a maximum RH is maintained whilst the set is placed in a stove for 28 days at 60°C. The metal specimen is subsequently evaluated.

Pewter, Pewterer: tin and tin-based alloys, craftsman using pewter to produce objects

Pig lead: crude lead first obtained from a smelting furnace

Pitch: a resin originating from plants, like tar, bitumen or asphalt

Plane (to-), Planing: flattening of a metal surface using abrasive techniques (e.g. milling)

Press (to-), Pressing: plastic deformation of a metal by using a die, mostly on sheet metal

Punch: steel rod with the face of a character, cut by a punchcutter

Red brass: brass alloys with maximum of about 15 wt% zinc; sometimes used for Cu-Zn-Sn alloys

Roasting: heating an ore until the metal content is released

Segregation: the selective parting of metals from a melt

Shellac: a resin produced from lac bugs (Kerria lacca), originating from India or Thailand

Shrinkage cavity: hole in a metal cast piece due to the shrinkage of the metal upon solidification

Sink (to-), Sinking: Impressing a punch in a soft metal by using a hammer or press

Solid solution: distribution of elements in a solidified solution such as a cast metal piece

Solution: dispersion of elements in a liquid solution

Stamp (to-), Stamping: similar to pressing

Strike: a copper (or copper alloy) piece with the negative imprint of a punch

Ternary alloys: composed of three metals

Type, Types: Lead based alloy letters to print

Wet (to-), Wetting: making a surface adhere to a liquid (i.e. water, a solution or a molten metal)

x-height: height dimension of the letter x within an alphabet or fount

3 Publications 2013-2017 (A 1, P 1)

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4 Chapter 1, List of strikes and matrices

All strikes and matrices in the MPM collection were counted and photographed. With some sets, the number of strikes/matrices does not correspond with the information from the Inventory of Parker-Melis ('#PM strikes/matrices') or the numbers ('# Web') and description ('Title') which are present on the museum website. The deviating numbers are marked red in the column '# count'. The column '# XRF' indicates the number of strikes/matrices that were measured in this project, using XRF.

MA number	Inv. P-M	Creator / attributed to	Year Cat. 2016	#PM stri-kes	#PM ma-trices	# Web	# count	# XRF	Title
MA.001.a	6	Keere, Hendrik v d	1570		26	6	27	27	6 'Grasses Capitales de 3 R Mediane'
MA.001.b	7	Keere, Hendrik v d	1573		69	69	71	71	69 'Gras Canon Romain'
MA.002	8	Garamont, Claude	1549		137	137	82	82	137 'Gros Canon Romain'
MA.003.a	8	Garamont, Claude	1549				55	55	'Gros Canon Romain'
MA.003.b	13	Keere, Hendrik v d	1571		23	23	23	23	23 'Moyen Canon Romain'
MA.004	128	Keere, Hendrik v d	1570		65	65	61	61	65 'Canon Flamand'
MA.005.a	126		1400-1599		21	21	21	21	21 'Canon Capitales Lombardes'
MA.005.b	9		1400-1599		23	23	23	23	23 'Capitales de 2 R Augustine'
MA.006	188	Bé, Guillaume Le (I)	1559		33	33	33	33	33 'Gros Hebreu Fort Gros'
MA.007	22	Granjon, Robert	1569		127	127	125	10	127 'Ascendonica Romaine'
MA.008	22	Granjon, Robert	1569-1570		160	160	160	8	160 'Ascendonica Romaine'
MA.009	3	Garamont, Claude	1567		23	23	23	23	23 'Grosses Capitales Extraordinaires'
MA.010	4		1700-1799		28	28	28	28	28 'Capitales de 3 R Augustine'
MA.011	88	Granjon, Robert	1570		125	125	125	125	125 'Ascendonica Cursive'
MA.012	25	Keere, Hendrik v d	1575		121	121	121	0	121 'Reale Romaine'
MA.013	133	Keere, Hendrik v d	1570		97	97	97	0	97 'Parangonne Flamande'
MA.014	28	Granjon, Robert	1566		120	120	120	0	120 'Parangonne Romaine'
MA.015	90	Granjon, Robert	1554		162	162	163	163	162 'Parangonne Cursive'
MA.016	173	Granjon, Robert	1565	3	233	116	120	0	116 'Parangonne Grecque'
MA.017	173	Granjon, Robert	1565			112	116	0	112 'Parangonne Grecque'
MA.018	190	Bé, Guillaume Le (I)	1566		38	38	38	38	38 'Double Parangonne Hébrue'
MA.019	29 B		1500-1599		101	101	101	0	101 'Texte Romain'
MA.020.a	30	Garamont, Claude	1549		176	88	172	172	88 'Texte Romain'
MA.020.b	30	Garamont, Claude	1564			88	5	5	88 'Texte Romain'
MA.020.c	35	Keere, Hendrik v d	1569-1570		15	20	15	15	20 'Nouveau Texte Romain'
MA.020.d	30	Garamont, Claude	1564		22	22	21	21	22 'Texte Romain, fragment'
MA.021	137		1567		122	122	122	65	122 'Augustine Allemande'
MA.022.a	92	Granjon, Robert	1562		103	103	103	103	103 'Texte Cursive'
MA.023	92	Granjon, Robert	1562	30		30	30	30	30 'Texte Cursive'
MA.022.b	93	Smit, Johan Michael	1564		31	31	31	31	31 'Texte Capitales Cursives'
MA.024	205		1517 circa		90	90	90	90	90 'Petit Texte Hebrue'
MA.025.a	38	Garamont, Claude	1556		203	203	203	178	203 'Augustine Romaine'
MA.025.b	53	Granjon, Robert	1569		22	22	22	22	22 'Augustine Romaine sur mediane'
MA.025.c	40	Smit, Johan Michael	1736		12	12	12	12	12 'Augustine Romaine'
MA.026.a	53 A	Granjon, Robert	1569		128	128	128	128	128 'Mediane Romaine'

MA.026.b	40	Smit, Johan Michael	1736		12	12	12	12	12 'Augustine Romaine'
MA.027.a	97	Granjon, Robert	1543		112	112	112	112	112 'Augustine Cursive Première'
MA.027.b	99		1700-1799		17	17	17	17	17 'Augustine Cursive'
MA.027.c	98	Smit, Johan Michael			8	8	8	8	8 'Augustine Cursive'
MA.027.d	51		1500-1599		9	9	9	9	9 'Augustine Chiffres'
MA.028	96	Granjon, Robert	1563		135	135	135	135	135 'Augustine Cursive'
MA.029	107		1500-1599		128	128	128	0	128 'Mediane Cursive'
MA.030	138	Keere, Hendrik v d	1570-1572		71	71	71	10	71 'Augustine Flamande'
MA.031	89	Guyot, François	1557		105	105	105	105	105 'Ascendonica Cursive'
MA.032	176	Haultin, Pierre	1560		297	150	141	10	150 'Augustine Grecque'
MA.033	176	Haultin, Pierre	1560			150	154	0	150 'Augustine Grecque'
MA.034	193		1523		45	45	45	45	45 'Double Augustine Hebrue'
MA.035	41	Wolsschaten, J-B. van	1760 circa		153	153	153	153	153 'Augustine Romaine'
MA.036.a	54	Garamont, Claude	1552		195	195	195	85	195 'Mediane Romaine'
MA.036.b	60	Granjon, Robert	1566		21	21	21	21	21 'Mediane Romaine sur Philosophie'
MA.037	110	Granjon, Robert	1565		129	129	129	0	129 'Mediane Cursive Droite'
MA.038	165	Granjon, Robert	1556	9	126	126	135	0	126 'Mediane Lettre Françoise'
MA.039	143		1500-1599		85	85	85	0	85 'Philosophie Allemande'
MA.040	196	Bé, Guillaume Le (I)	1565-1566		57	57	57	57	57 'Double Mediane Hebreu'
MA.041	32	Smit, Johan Michael	1732-1736		77	77	76	0	77 'Texte Romain'
MA.042	139	Keere, Hendrik v d	1570-1571		71	71	71	0	71 'Mediane Flamande'
MA.043	62	Keere, Hendrik v d	1578		122	122	122	0	122 'Philosophie Romaine'
MA.044	142	Keere, Hendrik v d	1570		87	83	86	0	83 'Philosophie Flamande'
MA.045	70	Rosart, Jacques-François	1748-1752		180	180	180	12	180 'Garamonde Romaine'
MA.046	72	Rosart, Jacques-François	1758		196	196	196	196	196 'Colineus Romaine'
MA.047.a	67	Garamont, Claude	1562		180	180	181	181	180 'Garamonde Romaine'
MA.047.b	71	Granjon, Robert	1566		17	17	17	17	17 'Garamonde Romaine sur Colineus'
MA.047.c	69		1700-1799		11	11	11	11	11 'Garamonde Romaine'
MA.048.a,b	68	Garamont, Claude	1555		224	224	224	224	224 'Garamonde Romaine Première'
MA.049.a	113	Granjon, Robert	1577		135	135	135	135	135 'Garamonde Cursive, la Valentine'
MA.049.b	113	Granjon, Robert	1577		22	22	22	22	22 'Garamonde Cursive, Valentine Capitales'
MA.050	167	Granjon, Robert	1566	17	62	62	79	0	62 'Garamonde Lettre Françoise'
MA.051	180	Granjon, Robert	1559		368	184	176	57	184 'Garamonde Grecque'
MA.052	180	Granjon, Robert	1559			184	192	54	184 'Garamonde Grecque'
MA.053.a	75	Tavernier, Ameet	1553		132	132	132	131	132 'Colineus Romaine'
MA.053.b	185	Garamont, Claude	1566		34	34	34	34	34 'Colineus Petites Capitales (Roman, Greek)'
MA.054.a	114	Granjon, Robert	1545		152	152	149	148	152 'Garamonde Cursive Première'
MA.054.b	115	Keere, Hendrik v d	1576		35	35	35	35	35 'Garamonde Cursive sur Colineus'
MA.055	36		1700-1799		65	65	65	0	65 'Augustine Romaine'
MA.056.a	77	Garamont, Claude	1553		173	173	173	173	173 'Bible Romaine'
MA.056.b	78		1600-1799		21	21	21	21	21 'Bible Romaine Fragment'
MA.057	77	Garamont, Claude	1553		165	165	165	165	165 'Bible Romaine'

MA.058.a	117	Granjon, Robert	1555		150	150	150	150	150 'Bible Cursive'
MA.058.b	119	Granjon, Robert	1600-1799		16	16	16	16	16 'Bible Cursive sur Jolie'
MA.059	183	Haultin, Pierre	1553		493	250	222	70	250 'Bible Grecque'
MA.060	183	Haultin, Pierre	1553			250	271	70	250 'Bible Grecque'
MA.061	76	Granjon, Robert	1570		123	123	123	0	123 'Gaillarde Romaine'
MA.062	81	Keere, Hendrik v d	1570-1573		164	164	165	88	164 'Coronelle Romaine'
MA.063	76	Granjon, Robert	1570		119	119	119	61	119 'Gaillarde Romaine'
MA.064.a	148		1572		84	84	83	0	84 'Colineus Flamande'
MA.064.b	149	Keere, Hendrik v d	1576		80	80	80	0	80 'Colineus Flamande'
MA.064.c	249		1576		16	16	16	0	16 'Colineus Signes de l' Almanach'
MA.064.d,e	249		1576		31	30	31	0	30 'Colineus Signes de l' Almanach'
MA.064.f	249		1576		3	3	3	0	3 'Colineus Signes de l' Almanach'
MA.065	83	Haultin, Pierre	1553		119	119	119	0	119 'Petite Nompareille Romaine'
MA.066.a	121	Haultin, Pierre	1557		110	110	110	110	110 'Nompareille Cursive'
MA.066.b	253		1563		10	10	10	10	10 'Nompareille Cursive Chiffres Encirclées'
MA.067	83	Haultin, Pierre	1553		135	135	136	57	135 'Petite Nompareille Romaine'
MA.068	156	Keere, Hendrik v d	1569		84	84	84	84	84 'Nompareille Flamande'
MA.069	94	Guyot, François	1547		122	122	122	120	122 'Texte Cursive'
MA.070	82	Keere, Hendrik v d	1575		126	126	126	126	126 'Jolie Romaine'
MA.071	120	Granjon, Robert	1572		137	137	137	136	137 'Jolie Cursive'
MA.072	202	Bé, Guillaume Le (I)	1560 circa		78	78	79	79	78 'Vrai Texte Hebreu, Façon de Venise'
MA.073.a	219	Hondius, Judocus	1591-1595		63	63	63	63	63 'Texte Aethiopique'
MA.073.b	220	Hondius, Judocus	1591-1595		22	63	22	22	63 'Texte Samaritain'
MA.074.a	55		1500-1599		122	122	122	0	122 'Mediane Romaine'
MA.074.b	240		1500-1599		17	17	17	0	17 'Chiffres et Capitales lignées pour musique'
MA.075	56	Haultin, Pierre	1548		67	67	67	0	67 'Mediane Romaine'
MA.076	82	Keere, Hendrik v d	1575		126	126	126	126	126 'Jolie Romaine'
MA.077	20	Tavernier, Ameet	1552		117	177	117	117	177 'Petit Petit Canon Romaine'
MA.078	3	Garamont, Claude	1567		37	37	37	37	37 'Grosses Capitales Extraordinaires'
MA.079.a	14	Keere, Hendrik v d	1571	1	26	26	26	26	26 'Capitales de 2 R Mediane'
MA.079.b	21	Garamont, Claude	1562		26	26	26	26	26 'Capitales de 2 R Bible'
MA.080.a	33		1500-1599		113	113	113	0	113 'Texte Romain'
MA.080.b	34		1500-1599		10	10	10	0	10 'Texte Chiffres'
MA.080.c	44		1500-1599		23	23	23	0	23 'Augustine Petites Capitales'
MA.080.d	66		1500-1599		24	24	24	0	24 'Garamonde Romaine Capitales'
MA.081	92	Granjon, Robert	1562		156	156	155	0	156 'Texte Cursive'
MA.082.a	215	Bé, Guillaume Le (I)	1569-1570		36	36	36	36	36 'Coronelle Hebreu'
MA.082.b	198		1500-1599		61	61	193	0	61 'Parangonne Hebreu'
MA.082.c	210		ca 1517-1566		33	33		0	33 'Petite Augustine Hebreu Cursive'
MA.082.d	207		onbekend		57	57		0	57 'Augustine Vieille Hebreu'
MA.082.e	207		1400-1599		42	42		0	42 'Augustine Vieille Hebreu'
MA.083.a	215	Bé, Guillaume Le (I)	1569-1570		30	30	30	30	30 'Coronelle Hebreu'
MA.083.b (d)	214	Picard, Jean Arnoul (jeune)	1565	10	38	38	48	48	38 'Hebreu sur la Garamonde et Bible'
MA.083.c	197		1500-1599		17	17	17	17	17 'Double Mediane vowels, intonations'

MA.084.a	28	Granjon, Robert	1566		26	26	26	0	26 'Parangonne Capitales'
MA.084.b	45	Haultin, Pierre	1549		11	11	11	0	11 'Augustine Capitales Fragment'
MA.084.c	140		1500-1599		19	19	19	0	19 'Mediane Capitales Flamande'
MA.085	229	Keere, Hendrik v d	1570-1571		38	38	31	0	38 'Petites Notes du Missel'
MA.086	225	Granjon, Robert	1570		20	20	20	0	20 'Premières Notes'
MA.087	226	Keere, Hendrik v d	1571-1572		41	41	41	0	41 'Moyennes Notes du Missel'
MA.088	227	Keere, Hendrik v d	1573		34	34	34	0	34 'Petites Notes pour les Processionels'
MA.089.a	223	Keere, Hendrik v d	1573-1574		22	22	20	0	22 'Moyennes Notes d' Espaigne'
MA.089.b	228		ca 1500-1599		19	19	19	0	19 'Moyennes Musique'
MA.090	224	Keere, Hendrik v d	1570-1571		32	32	32	0	32 'Grosses Notes de l' Antiphonaire'
MA.091.a	234	Keere, Hendrik v d	1577		63	63	66	66	63 'Grande Musique'
MA.091.b	233	Keere, Hendrik v d	1573		11	11	7	7	11 'Grosses Notes'
MA.092.a	240	Tavernier, Ameet	1554		69	69	68	0	69 'Moyennes Musique'
MA.092.b	239		1500-1599		70	70	70	0	70 'Moyennes Musique'
MA.092.c	238		1500-1599		23	23	23	0	23 'Moyennes Musique'
MA.092.d	230	Keere, Hendrik v d	1571		3	3	3	3	3 'Petites Notes entre lignes de l' Ascendonica'
MA.092.e	231	Keere, Hendrik v d	1572		3	3	3	3	3 'Petites Notes entre lignes de la Mediane'
MA.093	222	Keere, Hendrik v d	1573-1574		20	20	20	20	20 'Grosses Notes d' Espaigne'
MA.094	186	Granjon, Robert	1574-1575	186	44	22	187	0	22 'Jolie Grecque'
MA.095	186	Granjon, Robert	1574-1575			22	44	0	22 'Jolie Grecque'
MA.096	135	Keere, Hendrik v d	1570		113	113	113	112	113 'Texte Flamand'
MA.097	27	Garamont, Claude	1557		153	153	152	64	153 'Parangonne Romaine'
MA.098	26	Haultin, Pierre	1565		23	23	23	0	23 'Parangonne Capitales'
MA.099	111	Granjon, Robert	1565		135	135	135	0	135 'Philosophie Cursive'
MA.100	237	Keere, Hendrik v d	1578		67	67	67	0	67 'Moyenne Musique in 4°'
MA.101.a	235		1500-1599		31	31	31	0	31 'Moyenne Musique'
MA.101.b	236		1500-1599		19	19	19	0	19 'Moyenne Musique Fragment'
MA.101.c	247	Granjon, Robert	1566		25	25	25	25	25 'Petite Musique sur le Gros Texte'
MA.102	237	Keere, Hendrik v d	1578	62		62	62	62	62 'Moyenne Musique in 4°'
MA.103	184		1500-1599	225		112	137	0	112 'Bible Grecque'
MA.104.a	184	Haultin, Pierre	1553			113	88	0	113 'Bible Grecque'
MA.104.b	53 A	Granjon, Robert	1569	13	16	16	29	0	16 'Mediane Romaine Fragment'
MA.105	30	Garamont, Claude	1564	166		83	87	0	83 'Texte Romain'
MA.106	30	Garamont, Claude	1564			83	79	0	83 'Texte Romain'
MA.107	165	Granjon, Robert	1556-1557	103		103	103	0	103 'Mediane Lettre Françoise'
MA.108	161	Granjon, Robert	1566-1567		180	180	180	0	180 'Texte Courant'
MA.109	162	Granjon, Robert	1567		60	60	60	0	60 'Texte Bastard'
MA.110	117	Granjon, Robert	1555	143		129	143	143	129 'Bible Cursive'
MA.111	106	Haultin, Pierre	1557	96	35	35	131	10	35 'Mediane Italique Grasse'
MA.112	28	Granjon, Robert	1566	116		116	116	0	116 'Parangonne Romaine'
MA.113	109	Granjon, Robert	1554		158	158	158	0	158 'Mediane Cursive Pendante'
MA.114	67	Garamont, Claude	1562		175	87	93	0	87 'Garamonde Romaine'
MA.115	67	Garamont, Claude	1562			87	82	0	87 'Garamonde Romaine'
MA.116	116	Granjon, Robert	1565	126	7	126	133	0	126 'Colineus Italique Poetique'
MA.117	129		1500 circa		87	87	85	85	87 'Moyen Canon Flamand'

MA.118	88	Granjon, Robert	1570	122		61	60	60	61 'Ascendonica Cursive'
MA.119	88	Granjon, Robert	1570			61	62	62	61 'Ascendonica Cursive'
MA.120	120	Granjon, Robert	1572	111		111	111	111	111 'Jolie Cursive'
MA.121	88	Granjon, Robert	1570	121		111	60	60	111 'Ascendonica Cursive'
MA.122	88	Granjon, Robert	1570			111	61	61	111 'Ascendonica Cursive'
MA.123	175		1500-1599		342	171	195	0	171 'Augustine Grecque'
MA.124	175		1500-1599			171	147	0	171 'Augustine Grecque'
MA.125	28	Granjon, Robert	1566	116		116	116	0	116 'Parangonne Romaine'
MA.126	116	Granjon, Robert	1565	137		137	137	62	137 'Colineus Italique Poetique'
MA.127	76	Granjon, Robert	1570	135		135	135	0	135 'Gaillarde Romaine'
MA.128	96	Granjon, Robert	1563		127	127	127	127	127 'Augustine Cursive'
MA.129	116	Granjon, Robert	1565		133	133	133	0	133 'Colineus Italique Poetique'
MA.130	217	Granjon, Robert	1569		147	147	147	0	147 'Augustine Syriaque'
MA.131.a	12	Schoeffer, Peter (de jonge)	1517		25	25	25	25	25 'Canon Capitales'
MA.131.b	11	Guyot, François	1546	2	51	51	53	53	51 'Canon Romain'
MA.132	134		1523		92	92	92	0	92 'Texte Flamand'
MA.133	108	Granjon, Robert	1548		120	120	120	0	120 'Mediane Cursive Première Maigre'
MA.134	120	Granjon, Robert	1572	111		111	111	111	111 'Jolie Cursive'
MA.135.a	208	Bé, Guillaume Le (I)	1574	39		39	39	39	39 'Augustine Cursive Hebraique'
MA.135.b	212		1665	34		34	34	34	34 'Mediane Cursive Hebraique'
MA.135.c	213		1565	29		29	29	29	29 'Garamonde Cursive Hebraique'
MA.136	125	Keere, Hendrik v d	1574	1	61	31	19	0	31 'Canon d' Espaigne'
MA.137	125	Keere, Hendrik v d	1574			31	44	0	31 'Canon d' Espaigne'
MA.138	163	Granjon, Robert	1565		76	76	76	0	76 'Augustine Lettre Françoise'
MA.139	172		1500-1599		11	11	11	0	11 'Petit Canon Capitales Grecques'
MA.140	182	Haultin, Pierre	1564		295	148	295	70	148 'Bible Grecque'
MA.141	182	Haultin, Pierre	1564	25		148	25	25	148 'Bible Grecque'
MA.142	179	Haultin, Pierre	1549		411	205	204	59	205 'Mediane Grecque'
MA.143	179	Haultin, Pierre	1549			205	208	61	205 'Mediane Grecque'
MA.144	90	Granjon, Robert	1554	143	3	72	60	60	72 'Parangonne Cursive'
MA.145	90	Granjon, Robert	1554			72	86	86	72 'Parangonne Cursive'
MA.146	105	Tavernier, Ameet	1553	126		126	126	126	126 'Mediane Cursive'
MA.147	112	Granjon, Robert	1559	99		99	99	59	99 'Garamonde Cursive, l' Immortelle'
MA.148	81	Keere, Hendrik v d	1570-1573	151		151	151	59	151 'Coronelle Romaine'
MA.149	174	Garamond, Claude	1562		26	26	26	0	26 'Parangonne Capitales Grecques'
MA.150	43		1500-1599	103		103	103	0	103 'Augustine Romaine'
MA.151	70	Rosart, Jacques-François	1748-1752	13	15	15	28	28	15 'Garamonde Romaine Fragment'
MA.152	160		1500-1599		82	82	82	0	82 'Ascendonica Civilité'
MA.153	94	Guyot, François	1547	110		110	110	110	110 'Texte Cursive'
MA.154.a	49		1500-1599		8	8	8	0	8 'Augustine Romaine Fragment'
MA.154.b	58		1400-1599			24	24	0	24 'Mediane Capitales Romaines'
MA.154.c	79	Haultin, Pierre	1555	10		10	10	0	10 'Bible Capitales Fragment'
MA.155	194		1500-1599	27		27	27	0	27 'Double Augustine Hebreu Ashkenazi'
MA.156	120	Granjon, Robert	1572	77		77	77	77	77 'Jolie Cursive'
MA.157	18		1500-1599		51	51	51	0	51 'Petit Canon Romain'

MA.158	164	Haultin, Pierre	1561		88	88	88	10	88 'Petite Augustine Françoise'
MA.159	76	Granjon, Robert	1570	97	2	2	99	0	2 'Gaillarde Romaine'
MA.160	80	Haultin, Pierre	1555		153	153	153	90	153 'Coronelle, Grosse Nompareille Romaine'
MA.161	81	Keere, Hendrik v d	1570-1573		157	157	157	67	157 'Coronelle Romaine'
MA.162	252		1500-1599	9		9	9	0	9 'Coronelle Chiffres Soulignées'
MA.163	159	Tavernier, Ameet	1559		88	88	88	88	88 'Ascendonica Civilité'
MA.164.a	200		1500-1599	23		23	23	5	23 'Vrai Texte Hebreu'
MA.164.b	211		1500-1599	29		29	29	0	29 'Mediane Hebreu'
MA.164.c	195	Hand A		24	2	2	26	5	2 'Double Augustine Hebreu vowels, intonations'
MA.165	132		1600-1699		75	75	75	0	75 'Parangonne Flamande'
MA.166	37		1500-1599		73	37	73	0	37 'Grosse Augustine Romaine'
MA.167.a	199		1665		29	29	29	29	29 'Vrai Texte Hebreu'
MA.167.b	189		1500-1599	15		15	15	15	15 'Double Parangonne Hebreu Ashkenazi'
MA.168	63		1500-1599		17	17	17	0	17 'Philosophie Capitales Romaines'
MA.169.a	50		1500-1599		24	24	24	0	24 'Augustine Capitales Romaines'
MA.169.b	95		1500-1599		30	30	30	0	30 'Augustine Cursive Fragment'
MA.169.c	104	Granjon, Robert	1548		7	7	7	0	7 'Mediane Cursive Fragment'
MA.169.d	141		1500-1599		16	16	16	0	16 'Philosophie Flamande Fragment'
MA.169.e	151		1500-1599		6	6	6	0	6 'Bible Flamande Fragment'
MA.169.f	250	Keere, Hendrik v d		12		12	12	0	12 'Signes'
MA.170	131		1500-1599		54	54	54	0	54 'Ascendonica Flamande'
MA.171	136	16de eeuw	1500-1599		69	69	69	8	69 'Augustine Flamande'
MA.172.a	46		1500-1599		15	5	15	15	15 'Augustine Romaine Fragment'
MA.172.b	47		1500-1599		11	11	11	11	11 'Augustine Romaine Fragment'
MA.172.c	48		1500-1599		8	8	8	8	8 'Augustine Romaine Fragment'
MA.172.d	178		1500-1599		15	15	15	15	15 'Mediane Grecque Fragment'
MA.172.e	102		1500-1599		26	26	26	26	26 'Mediane Cursive Fragment'
MA.172.f	103		1500-1599		10	10	10	10	10 'Mediane Cursive Chiffres'
MA.172.g	91		1500-1599		9	9	9	9	9 'Parangonne Cursive Chiffres'
MA.173.a	201		1500-1599	17	11	11	28	0	11 'Vrai Texte Hebreu'
MA.173.b	153		1520		24	24	24	0	24 'Bible Flamande Fragment'
MA.173.c	145		1500-1599		21	21	21	0	21 'Garamonde Flamande Fragment'
MA.174	85	Guyot, François	1543		43	43	43	42	43 'Moyen Canon Cursive'
MA.175.a	57		1500-1599		32	32	32	0	32 'Mediane Romaine Fragment'
MA.175.b	65		1500-1599		10	10	10	0	10 'Philosophie Chiffres'
MA.175.c	101		1500-1599		11	11	11	0	11 'Mediane Cursive Fragment'
MA.176	96	Granjon, Robert	1563	123		123	123	0	123 'Augustine Cursive'
MA.177.a	152		1500-1599		43	43	43	0	43 'Bible Flamande Fragment'
MA.177.b	206		1500-1599		26	26	26	0	26 'Petit Texte Hebreu Ashkenazi'
MA.178	31		1500-1599		57	57	57	0	57 'Texte Romaine'
MA.179	28	Granjon, Robert	1566	115		115	115	0	115 'Parangonne Romaine'
MA.180	191		1500-1599	45		45	45	0	45 'Double Texte Hebreu'
MA.181	192		1500-1599	45		45	45	0	45 'Double Texte Hebreu'
MA.182	88	Granjon, Robert	1570	122		61	61	61	61 'Ascendonica Cursive'
MA.183	88	Granjon, Robert	1570			61	61	60	61 'Ascendonica Cursive'
MA.184	120	Granjon, Robert	1572	111		111	111	111	111 'Jolie Cursive'

MA.185	177		1500-1599	181		90	101	0	90 'Mediane Grecque'
MA.186	177		1500-1599			90	80	0	90 'Mediane Grecque'
MA.187	74	Granjon, Robert	1574	116		116	116	0	116 'Colineus Romaine, la Granjonne'
MA.188.a	254	Keere, Hendrik v d			2	2	2	2	2 'Fleuron sur 2 R Augustine'
MA.188.b	255	Keere, Hendrik v d			2	2	2	2	2 'Fleuron sur 2 R Mediane'
MA.188.c	258	Keere, Hendrik v d			2	2	2	2	2 'Fleuron sur la Parangonne'
MA.188.d	258	Keere, Hendrik v d			2	2	2	2	2 'Fleuron sur la Parangonne'
MA.188.e	258	Keere, Hendrik v d			2	2	2	2	2 'Fleuron sur la Parangonne'
MA.188.f	259	Granjon, Robert			4	2	2	2	2 'Fleuron sur le Texte'
MA.188.g	259	Granjon, Robert				2	2	2	2 'Fleuron sur le Texte'
MA.188.h	265	Keere, Hendrik v d			4	2	2	2	2 'Fleuron sur la Mediane'
MA.188.i	265	Keere, Hendrik v d				2	2	2	2 'Fleuron sur la Mediane'
MA.188.j	269		1500-1599		1	1	1	1	1 matrijs 'Fleuron sur le Petit Canon'
MA.188.k	271		1500-1599		2	2	2	2	2 'Fleuron sur le Texte'
MA.188.l	272	Garamont, Claude			1	1	1	1	1 matrijs 'Fleuron sur l' Augustine'
MA.188.m	276	Keere, Hendrik v d	1570		2	2	2	2	2 'Fleuron sur la Coronelle'
MA.188.n	276	Keere, Hendrik v d	1570		2	2	2	2	2 'Fleuron sur la Coronelle'
MA.188.o	276	Keere, Hendrik v d	1570		2	2	2	2	2 'Fleuron sur la Coronelle'
MA.188.p	270		1500-1599	1		1	1	1	1 matrijs 'Fleuron sur l' Ascendonica'
MA.188.q	273		1500-1599		1	1	0	0	1 matrijs 'Fleuron sur l' Augustine'
MA.188.r	274			1		1	1	1	1 matrijs 'Fleuron sur la Mediane'
MA.188.s	275		1500-1599		1	1	1	1	1 matrijs 'Fleuron sur la Garamonde'
MA.189	118	Granjon, Robert	1555	124		124	124	0	124 'Coronelle Cursive, la Mignonne'
MA.190	130		1536		62	62	62	0	62 'Ascendonica Flamande'
MA.191	120	Granjon, Robert	1572	111		111	111	111	111 'Jolie Cursive'
MA.192	84			5	150	75	93	0	75 'Roman Pool'
MA.193	84					75	61	0	75 'Roman Pool'
MA.194	122			4	28	28	32	0	28 'Italic Pool'
MA.195.a	158				23	23	23	0	23 'Gothic Pool'
MA.195.b	187			2	3	3	5	0	3 'Greek Pool'
MA.195.c	216				1	1	1	0	1 matrijs 'Hebrew Pool'
MA.196.a	232				38	38	38	0	38 'Music Pool (two printing)'
MA.196.b	248				20	20	20	0	20 'Music Pool (one printing)'
MA.197	288			5	105	34	109	0	34 'Miscellaneaous Pool'
MA.198	288				8	34	8	0	34 'Miscellaneaous Pool'
MA.199						0			Leeg
MA.200						0			Leeg
				4485	16011	20062	20498	8864	
				#PM:	20496				

5 Chapter 4 (3.1.4, 3.1.5): Tables of XRF- and SEM-EDX quantative results

5.1 Innov-X α-4000

Comparison table between the theoretical composition and weighted parts for composing the alloys and the software results of the portable Innov-X α-4000.

Alloy nrs.	GIVEN			INNOV-X 4000 Results		
	Pb	Sb	Sn	Pb	Sb	Sn
100 0 0	100	0	0	100.0	0.0	0.0
96 4 0	96	4	0	98.0	2.0	0.0
92 8 0	92	8	0	95.8	4.2	0.0
88 8 4	88	8	4	92.4	4.3	3.3
84 8 8	84	8	8	89.3	4.2	6.4
80 8 12	80	8	12	85.9	4.4	9.7
88 12 0	88	12	0	93.7	6.3	0.0
84 12 4	84	12	4	88.7	6.3	5.0
80 12 8	80	12	8	87.0	6.3	6.7
76 12 12	76	12	12	85.6	6.7	7.7
84 16 0	84	16	0	90.4	9.6	0.0
80 16 4	80	16	4	87.0	9.3	3.5
76 16 8	76	16	8	83.2	9.5	7.4
72 16 12	72	16	12	78.8	9.8	11.2
80 10 10	80	10	10	86.5	5.4	8.2
80 20 0	80	20	0	87.7	12.0	0.0

5.2 Niton XL3

Comparison table between the theoretical composition and the software results of the portable Niton XL3 XRF equipment.

Alloy numbers	Elements wt% theoretical			Elements wt% by XRF Niton		
	Pb	Sb	Sn	Pb	Sb	Sn
100 0 0	100	0	0	99.79	0.00	0.00
96 4 0	96	4	0	96.84	3.11	0.00
92 8 0	92	8	0	93.28	6.56	0.00
88 12 0	88	12	0	90.20	9.65	0.00
84 16 0	84	16	0	85.67	13.79	0.00
88 8 4	88	8	4	89.73	6.62	3.64
84 12 4	84	12	4	86.66	9.54	3.53
80 16 4	80	16	4	82.17	13.87	3.81
84 8 8	84	8	8	86.40	6.56	6.88
80 12 8	80	12	8	83.36	9.50	7.00
76 16 8	76	16	8	78.43	13.83	7.70
80 8 12	80	8	12	82.89	6.54	10.57
76 12 12	76	12	12	79.27	9.94	10.66
72 16 12	72	16	12	74.49	13.98	11.37
80 10 10	80	10	10	82.64	8.21	8.79
80 20 0	80	20	0	81.61	17.84	0.03

5.3 InnovX-Olympus Delta Professional

Comparison table between the given alloys and the software results of the portable Innov-X Delta equipment.

Alloy numbers	Elements wt% theoretical			Elements wt% by XRFInnov-X Delta		
	Pb	Sb	Sn	Pb	Sb	Sn
100 0 0	100	0	0	99.99	0.01	0.00
96 4 0	96	4	0	95.86	4.14	0.00
92 8 0	92	8	0	91.94	8.06	0.00
88 12 0	88	12	0	87.35	12.65	0.00
84 16 0	84	16	0	83.74	16.26	0.00
80 20 0	80	20	0	78.53	21.47	0.00
88 8 4	88	8	4	87.61	8.25	4.14
84 8 8	84	8	8	83.70	8.14	8.16
80 8 12	80	8	12	79.37	8.04	12.59
84 12 4	84	12	4	84.33	11.70	3.97
80 12 8	80	12	8	80.28	11.62	8.10
76 12 12	76	12	12	75.21	12.12	12.67
80 16 4	80	16	4	79.46	16.42	4.12
76 16 8	76	16	8	74.66	16.61	8.73
72 16 12	72	16	12	70.57	16.57	12.86

5.4 SEM EDX

Quantative results of the SEM Quanta 350 with Oxford Instruments EDX and INCA software.

Alloy nrs.	WEIGHTED			SEM-EDX		
	Pb	Sb	Sn	Pb	Sb	Sn
100 0 0	100	0	0	100.0	0.0	0.0
96 4 0	96	4	0	94.7	5.3	0.0
92 8 0	92	8	0	88.7	11.3	0.0
88 8 4	88	8	4	82.8	11.0	6.2
84 8 8	84	8	8	79.5	10.3	10.2
80 8 12	80	8	12	71.9	11.2	16.8
88 12 0	88	12	0	84.0	16.0	0.0
84 12 4	84	12	4	79.5	15.4	5.2
80 12 8	80	12	8	76.1	14.7	9.2
76 12 12	76	12	12	68.7	15.9	15.5
84 16 0	84	16	0	74.7	25.3	0.0
80 16 4	80	16	4	70.3	24.5	5.3
76 16 8	76	16	8	66.8	22.0	11.2
72 16 12	72	16	12	61.8	22.0	16.2

6 Chapter 4: SEM-EDX results on reference alloys

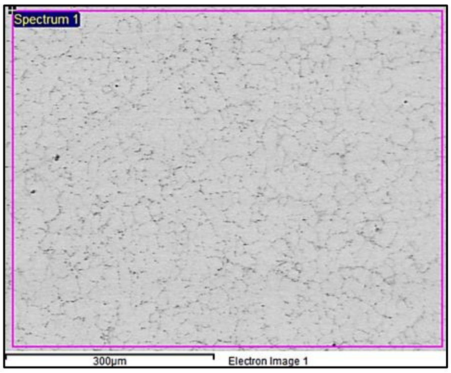


Fig. 6.1: Alloy 96-04-00 showing an evenly distribution of segregated Sb from the Pb rich grain boundaries

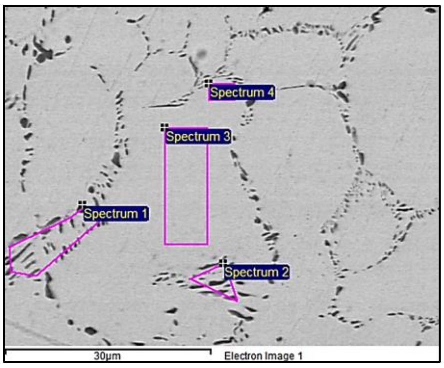


Fig. 6.2: Phase compositions (wt%):

Spect.	Sb	Pb
1	16.9	83.1
2	21.7	78.3
3	2.1	97.9
4	3.0	97.1

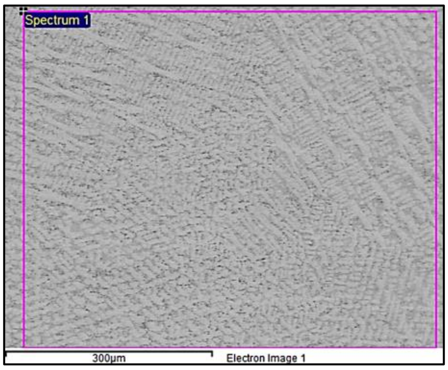


Fig. 6.3: Alloy 92-08-00

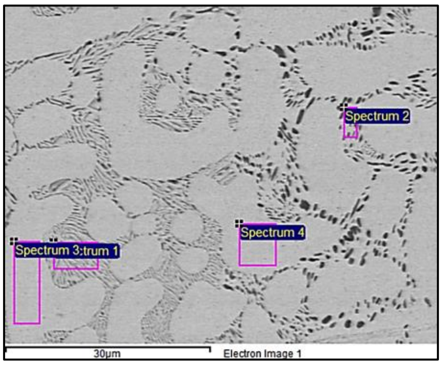


Fig. 6.4: Phase compositions (wt%):

Spect.	Sb	Pb
1	18.8	81.2
2	24.6	75.4
3	3.7	96.3
4	3.5	96.5

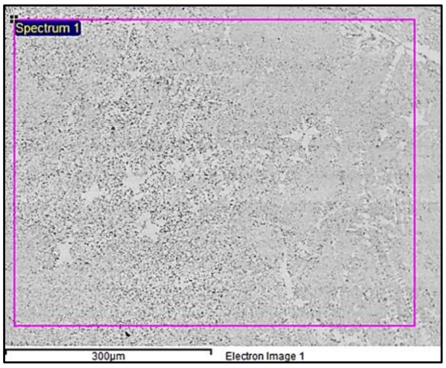


Fig. 6.5: Alloy 88-12-00

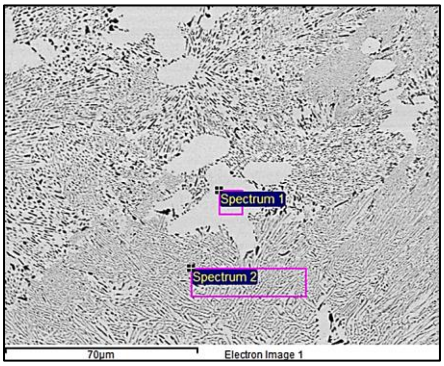


Fig. 6.6: Phase compositions (wt%):

Spect.	Sb	Pb
1	4.3	95.7
2	15.9	84.1

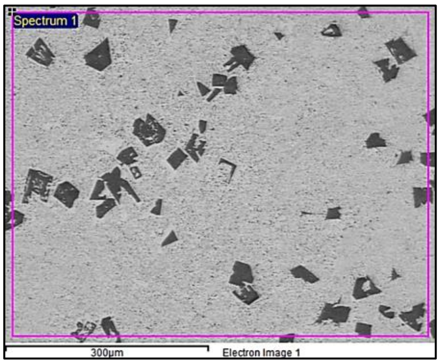


Fig. 6.7: Alloy 84-16-00

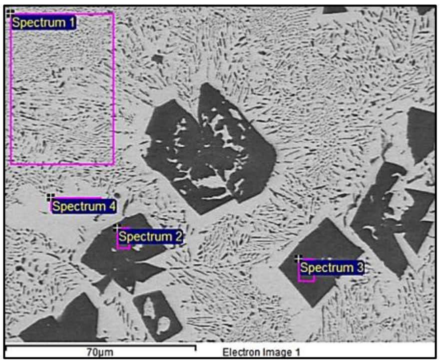


Fig. 6.8: Phase compositions (wt%):

Spect.	Sb	Pb
1	16.2	83.8
2	91.3	8.7
3	91.9	8.1
4	4.3	95.7

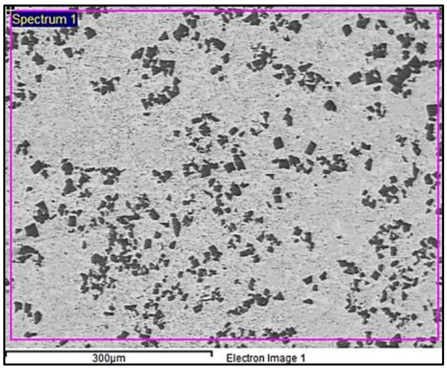


Fig. 6.9: Alloy 80-20-00

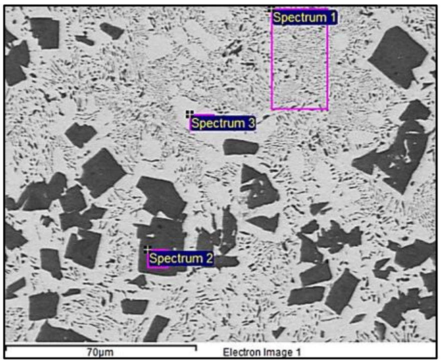


Fig. 6.10: Phase compositions:

Spect.	Sb	Pb
1	17.95	82.05
2	93.76	6.24
3	4.04	95.96

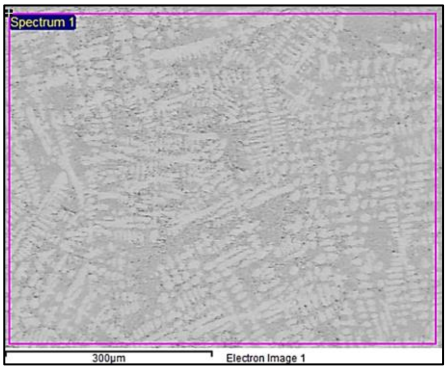


Fig. 6.11: Alloy 88-08-04

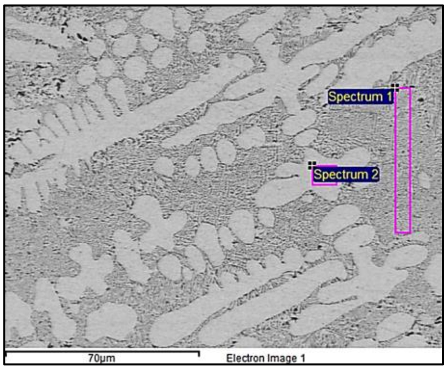


Fig. 6.12: Phase compositions:

Sp.	Sn	Sb	Pb
1	7.2	15.0	77.8
2	2.0	3.3	94.8

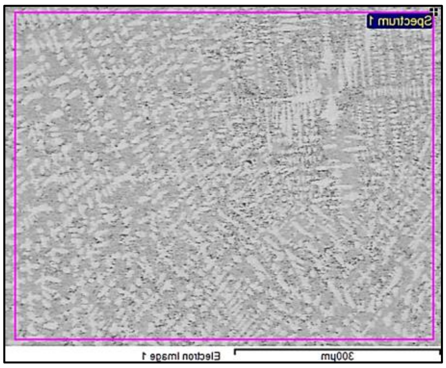


Fig. 6.13: Alloy 84-08-08

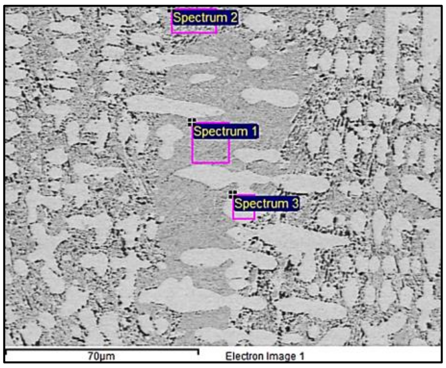


Fig. 6.14: Phase compositions (wt%):

Sp.	Sn	Sb	Pb
1	12.0	13.4	74.6
2	11.9	13.3	74.8
3	3.8	2.1	94.1

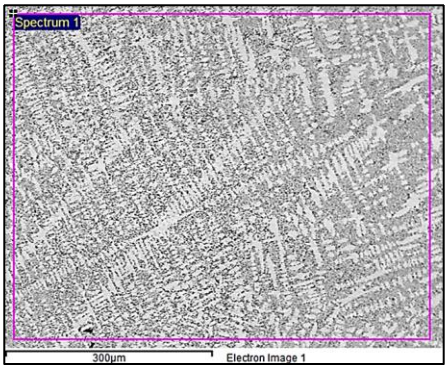


Fig. 6.15: Alloy 80-08-12

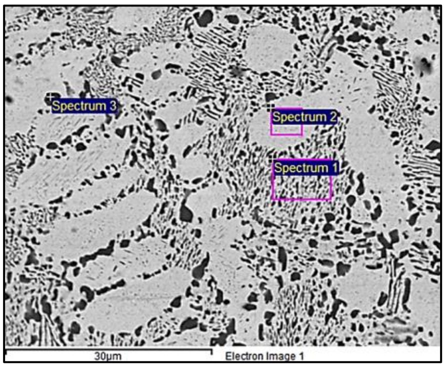


Fig. 6.16: Phase compositions:

Sp.	Sn	Sb	Pb
1	18.8	13.5	67.7
2	5.3	2.0	92.7
3	41.3	31.3	27.4

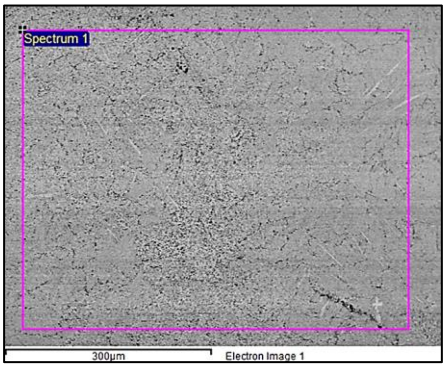


Fig. 6.17: Alloy 84-12-04

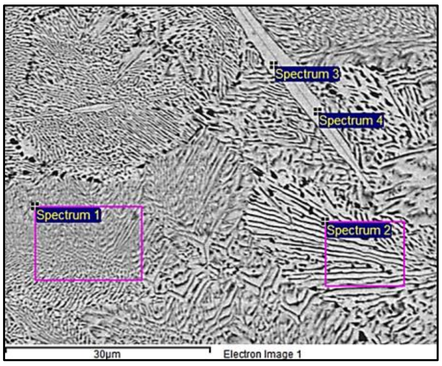


Fig. 6.18: Phase compositions:

Sp.	Sn	Sb	Pb
1	4.2	12.8	83.0
2	6.2	14.8	79.0
3	2.3	3.8	93.9
4	3.1	8.3	88.7

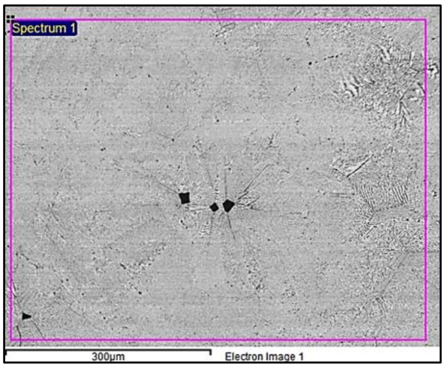


Fig. 6.19: Alloy 80-12-08

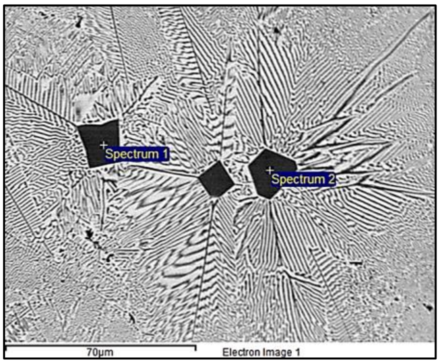


Fig. 6.20: Phase compositions:

Sp.	Sn	Sb	Pb
1	35.5	51.6	13.0
2	35.7	53.9	10.5

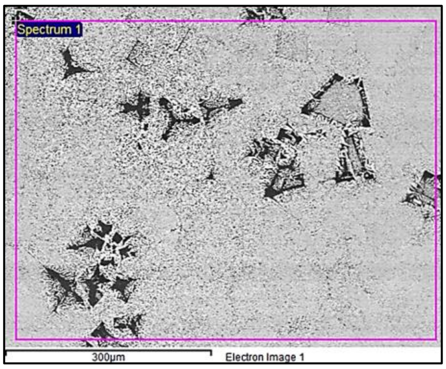


Fig. 6.21: Alloy 76-12-12

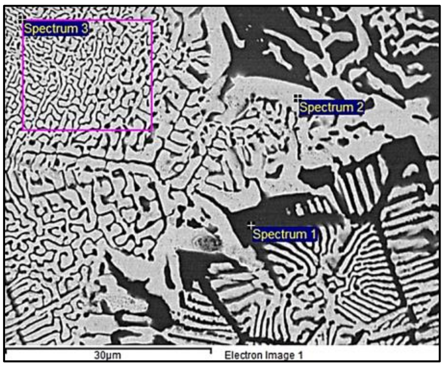


Fig. 6.22: Phase compositions:

Sp.	Sn	Sb	Pb
1	39.5	50.4	10.2
2	4.9	2.5	92.6
3	12.1	13.0	74.9

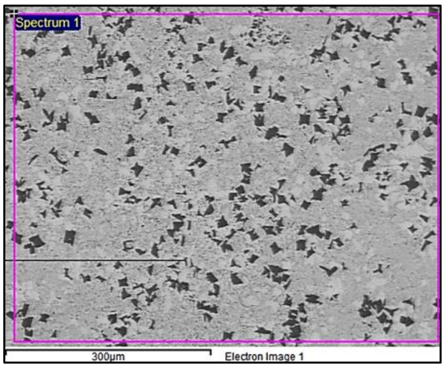


Fig. 6.23: Alloy 80-16-04

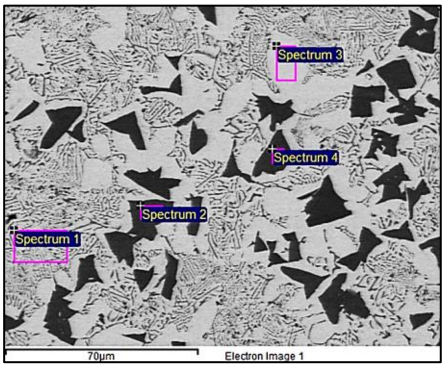


Fig. 6.24: Phase compositions:

Sp.	Sn	Sb	Pb
1	4.3	17.1	78.5
2	13.6	83.6	2.9
3	1.4	3.7	95.0
4	12.1	84.7	3.3

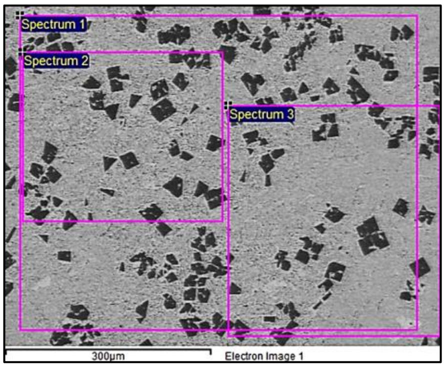


Fig. 6.25: Alloy 76-16-08

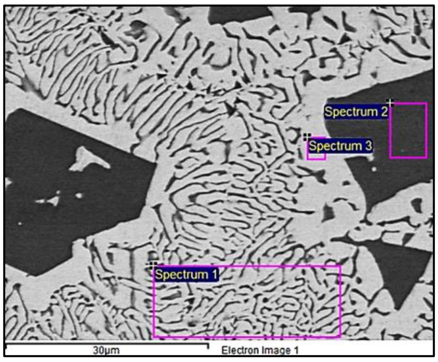


Fig. 6.26: Phase compositions:

Sp.	Sn	Sb	Pb
1	5.9	16.1	78.0
2	31.3	56.1	12.6
3	2.5	3.6	93.9

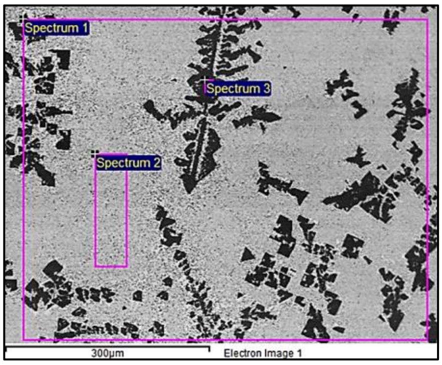


Fig. 6.27: Alloy 72-16-12

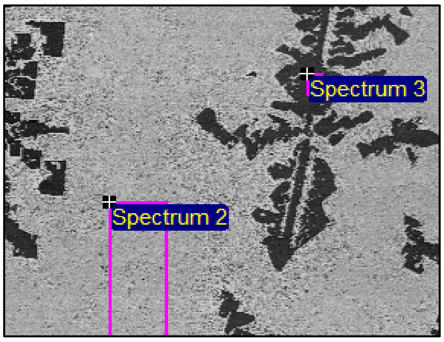


Fig. 6.28: Phase compositions, spectra taken from larger image (Fig. 6.27):

Sp.	Sn	Sb	Pb
1	Bulk		
2	10.0	12.8	77.3
3	35.4	51.2	13.4

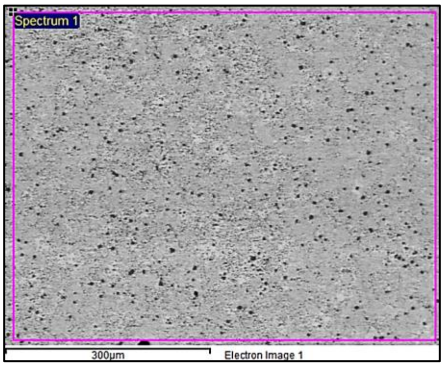


Fig. 6.29: Alloy 80-10-10 showing an evenly and fine distributed alloy with almost pure Pb, Pb-rich with equal wt% parts Sb-Sn (sub-eutectic binary alloy) and Sb-Sn rich phases.

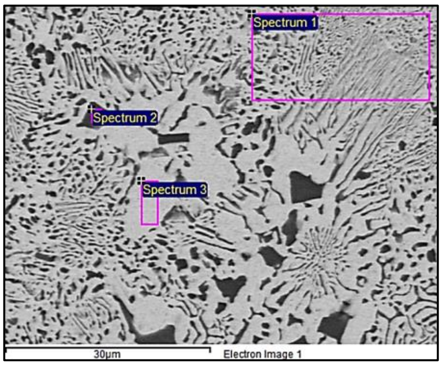


Fig. 6.30: Phase compositions:

Sp.	Sn	Sb	Pb
1	11.7	12.1	76.2
2	38.3	47.1	14.6
3	4.2	2.4	93.4

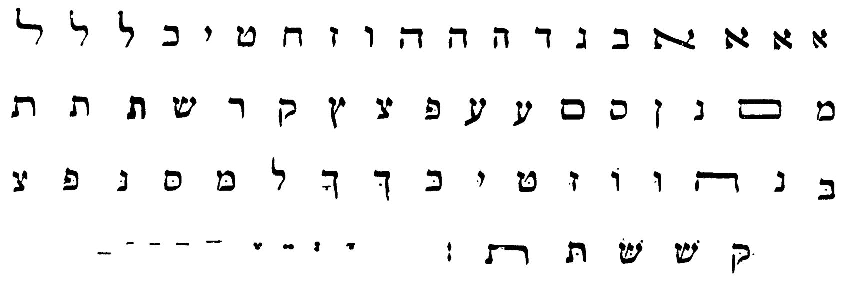
7 Chapter 4: Hebrew, Syriaque, Samaritain and Ethiopean types

Images of the types in Selection 3:

H I “Double Parangon Hebreu“, Le Bé.

H II “Double Augustine Hebreu“, v. 1523.

H III 2 regelen Mediaan, Le Bé.



H IV Text, Le Bé.

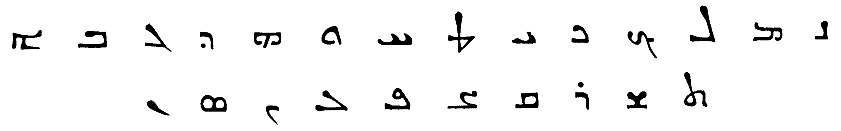
H V “Kleine Text“, v. 1517.

H VI “Augustine vieille Hebreu„ v. 1564.

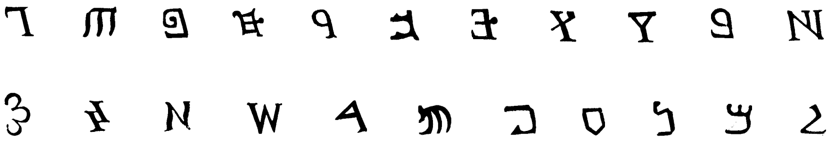
H VII “Hébreu sur la petite Augustine“, v. 1517.

H VIII Coronelle, Le Bé.

SY I Augustijn, Granjon.



SY II Augustijn Estrangelo, Granjon.



SA I Mediaan, einde 16e eeuw.

ET I Mediaan, einde 16e eeuw.

8 Chapter 5: List of statistical clustering results A

List of statistical clustering results for the measured sets of matrices

Results of the statistical grouping in 10 clusters (rows 1-10), showing the number of attribution of individual matrices in each set or subset.

Matrices	1	2	3	4	5	6	7	8	9	10
MA1a	23	1	1	1	1	0	0	0	0	0
MA1b	3	2	2	2	59	3	0	0	0	0
MA2	0	47	0	0	32	2	1	0	0	0
MA3	13	42	7	0	16	0	0	0	0	0
MA4	61	0	0	0	0	0	0	0	0	0
MA5a	0	0	0	21	0	0	0	0	0	0
MA5b	0	0	0	0	0	0	0	23	0	0
MA6	0	22	0	2	9	0	0	0	0	0
MA7	0	0	3	0	6	0	0	0	1	0
MA8	0	0	2	0	6	0	0	0	0	0
MA9	0	0	0	0	0	0	0	0	0	23
MA10	0	1	0	0	0	0	27	0	0	0
MA11	0	0	11	0	110	0	0	4	0	0
MA15	0	1	0	2	6	1	153	0	0	0
MA18	0	11	5	18	4	0	0	0	0	0
MA20a	3	4	0	86	24	3	16	36	0	0
MA20b	0	0	0	4	1	0	0	0	0	0
MA20c	0	1	0	2	5	0	1	5	1	0
MA20d	1	7	2	4	4	1	0	2	0	0
MA21	0	1	0	0	2	0	62	0	0	0
MA22a	0	0	3	97	3	0	0	0	0	0
MA22b	7	3	1	9	8	3	0	0	0	0
MA23	0	0	2	27	1	0	0	0	0	0
MA24	1	1	25	4	41	0	0	18	0	0
MA25a	1	7	18	4	41	6	0	100	1	0
MA25b	0	2	6	3	5	1	0	5	0	0
MA25c	0	4	0	4	2	0	0	1	1	0
MA26a	1	0	30	2	84	0	0	9	2	0
MA26b	0	0	4	0	7	0	0	0	1	0
MA27a	2	60	2	24	5	0	18	1	0	0
MA27b	0	2	0	0	0	0	0	0	15	0
MA27c	0	0	0	0	7	0	0	0	1	0
MA27d	0	0	0	0	9	0	0	0	0	0
MA28	0	0	2	13	118	0	0	0	2	0
MA30	0	1	0	0	2	0	0	7	0	0
MA31	1	2	5	0	63	4	0	29	0	0
MA32	0	9	0	1	0	0	0	0	0	0
MA34	0	1	0	0	31	0	0	13	0	0

MA35	0	0	0	1	1	0	0	0	151	0
MA36a	2	3	0	4	72	1	0	3	0	0
MA36b	1	3	0	16	1	0	0	1	0	0
MA40	0	54	0	2	1	0	0	0	0	0
MA45	0	0	0	0	0	0	0	0	12	0
MA46	0	61	0	0	0	0	0	0	135	0
MA47a	0	96	47	14	14	1	0	9	0	0
MA47b	0	11	0	6	0	0	0	0	0	0
MA47c	0	4	0	6	1	0	0	0	0	0
MA48a	2	11	1	75	64	4	0	38	0	0
MA48b	0	3	4	6	5	6	0	4	1	0
MA49a	0	30	30	43	31	0	0	1	0	0
MA49b	0	3	1	17	1	0	0	0	0	0
MA51	5	25	0	15	0	3	9	0	0	0
MA52	3	30	1	14	0	2	4	0	0	0
MA53a	0	1	4	1	123	0	0	2	0	0
MA53b	0	10	0	23	1	0	0	0	0	0
MA54a	0	45	0	17	44	0	0	42	0	0
MA54b	0	0	31	0	4	0	0	0	0	0
MA56a	19	5	2	20	10	111	0	2	4	0
MA56b	0	5	1	1	7	4	0	3	0	0
MA57	1	12	5	4	140	3	0	0	0	0
MA58a	0	77	1	21	3	3	44	0	1	0
MA58B	0	0	0	0	0	0	0	0	16	0
MA59	0	67	0	0	1	1	0	1	0	0
MA60	0	43	0	0	15	1	0	11	0	0
MA62	0	12	53	0	6	0	0	17	0	0
MA63	0	0	2	0	59	0	0	0	0	0
MA66a	0	71	1	29	0	2	0	7	0	0
MA66b	0	0	10	0	0	0	0	0	0	0
MA67	1	39	3	10	0	1	0	3	0	0
MA68	0	0	0	0	58	0	0	26	0	0
MA69	0	0	6	0	111	1	0	2	0	0
MA70	1	5	95	0	25	0	0	0	0	0
MA71	0	2	28	0	93	0	0	13	0	0
MA72	6	53	6	7	6	1	0	0	0	0
MA73a	0	5	33	0	25	0	0	0	0	0
MA73b	0	0	3	0	19	0	0	0	0	0
MA76	5	0	2	8	0	111	0	0	0	0
MA77	0	1	62	4	35	2	0	13	0	0
MA78	4	2	17	0	12	0	2	0	0	0
MA79a	0	0	0	1	25	0	0	0	0	0
MA79b	1	1	0	6	18	0	0	0	0	0
MA82a	23	0	0	0	13	0	0	0	0	0
MA83a	0	6	24	0	0	0	0	0	0	0

MA83b	0	0	26	0	1	9	0	2	0	0
MA83c	0	1	0	5	11	0	0	0	0	0
MA83d	0	0	0	0	0	10	0	0	0	0
MA91a	0	21	34	0	11	0	0	0	0	0
MA91b	0	0	1	0	6	0	0	0	0	0
MA92d	0	0	1	0	2	0	0	0	0	0
MA92e	0	0	2	0	1	0	0	0	0	0
MA93	1	2	15	0	2	0	0	0	0	0
MA96	45	0	2	0	65	0	0	0	0	0
MA97	0	23	17	20	0	0	0	4	0	0
MA101c	0	1	0	0	24	0	0	0	0	0
MA102	0	4	31	0	27	0	0	0	0	0
MA110	0	0	25	0	118	0	0	0	0	0
MA111	0	2	0	8	0	0	0	0	0	0
MA117	1	80	0	1	3	0	0	0	0	0
MA118	0	0	5	0	55	0	0	0	0	0
MA119	0	0	3	0	59	0	0	0	0	0
MA120	0	4	96	0	11	0	0	0	0	0
MA121	0	0	7	0	53	0	0	0	0	0
MA122	0	0	3	0	58	0	0	0	0	0
MA126	1	0	0	0	1	60	0	0	0	0
MA128	0	84	0	43	0	0	0	0	0	0
MA131a	0	10	0	0	0	15	0	0	0	0
MA131b	0	0	4	0	37	0	0	11	1	0
MA134	0	0	105	0	6	0	0	0	0	0
MA135a	0	0	24	0	10	0	0	5	0	0
MA135b	0	0	15	0	5	0	0	14	0	0
MA135c	0	0	2	0	11	0	1	15	0	0
MA140	1	9	5	53	1	0	0	1	0	0
MA141	0	15	1	9	0	0	0	0	0	0
MA142	0	46	4	9	0	0	0	0	0	0
MA143	0	48	8	5	0	0	0	0	0	0
MA144	0	0	35	0	25	0	0	0	0	0
MA145	0	5	55	0	26	0	0	0	0	0
MA146	1	0	109	0	16	0	0	0	0	0
MA147	0	0	0	0	0	0	59	0	0	0
MA148	0	3	39	0	17	0	0	0	0	0
MA151	0	0	0	0	0	0	0	0	28	0
MA153	0	4	83	2	20	0	0	1	0	0
MA156	0	2	67	0	8	0	0	0	0	0
MA158	0	0	0	10	0	0	0	0	0	0
MA160	0	0	49	2	6	0	0	33	0	0
MA161	15	1	20	0	17	0	0	14	0	0
MA163	11	1	4	0	70	0	0	1	1	0
MA164a	0	0	3	0	2	0	0	0	0	0

MA164c	0	0	3	0	0	0	0	2	0	0
MA167a	0	0	20	0	3	1	0	5	0	0
MA167b	0	9	0	0	0	6	0	0	0	0
MA171	0	1	0	0	6	0	0	1	0	0
MA172a	0	0	5	0	9	0	0	1	0	0
MA172b	0	0	10	0	1	0	0	0	0	0
MA172c	0	1	2	0	5	0	0	0	0	0
MA172d	0	0	0	0	15	0	0	0	0	0
MA172e	0	9	0	0	1	11	5	0	0	0
MA172f	0	3	1	6	0	0	0	0	0	0
MA172g	0	5	2	0	2	0	0	0	0	0
MA174	0	0	0	0	0	0	0	0	42	0
MA182	0	0	1	0	60	0	0	0	0	0
MA183	0	0	2	0	57	0	0	1	0	0
MA184	0	0	101	0	9	1	0	0	0	0
MA188	3	15	0	0	4	1	0	1	7	0
MA191	0	1	98	0	12	0	0	0	0	0

9 Chapter 5: List of statistical clustering results B

List of statistical clustering results for all individual matrices within the measured sets

Results of the statistical clustering for each individual matrix (Column ‘Cluster’). The quantitative XRF results for each measured element is given in the next columns (Pb, Sb, Sn, Zn, Fe, Ag, Ni, As). The last column (‘Original’) indicates whether the matrix is assumed to be original to the set or a later replacement or addition.

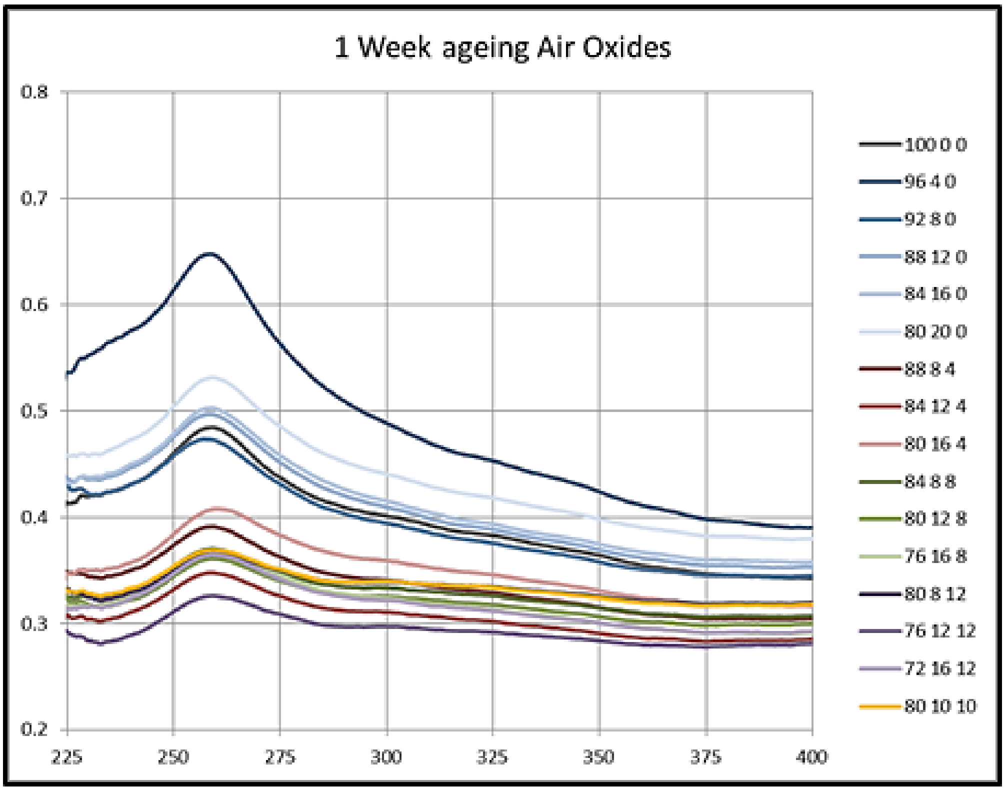
Matrix	Letter	Cluster	Pb	Sb	Sn	Zn	Fe	Ag	Ni	As	Original
MA1a	A	1	0.23	0.69	0.00	0.00	0.01	0.11	0.04	0.49	0
MA1a	B	1	0.21	0.60	0.00	0.00	0.02	0.11	0.04	0.37	0
MA1a	C	1	0.20	0.65	0.00	0.00	0.00	0.12	0.05	0.40	0
MA1a	D	1	0.15	0.64	0.00	0.00	0.02	0.12	0.05	0.40	0
MA1a	E	1	0.20	0.69	0.00	0.00	0.01	0.12	0.05	0.44	0
MA1a	F	1	0.18	0.65	0.00	0.00	0.00	0.12	0.04	0.41	0
MA1a	G	1	0.14	0.65	0.00	0.00	0.01	0.12	0.05	0.41	0
MA1a	H	1	0.17	0.70	0.00	0.00	0.00	0.13	0.05	0.41	0
MA1a	I	1	0.18	0.69	0.00	0.00	0.00	0.11	0.05	0.43	0
MA1a	K	1	0.16	0.65	0.00	0.00	0.01	0.11	0.04	0.38	0
MA1a	L	1	0.19	0.68	0.00	0.00	0.00	0.12	0.04	0.42	0
MA1a	M	1	0.16	0.58	0.00	0.00	0.00	0.11	0.05	0.33	0
MA1a	N	1	0.21	0.67	0.00	0.00	0.01	0.11	0.05	0.43	0
MA1a	O	1	1.22	0.70	0.00	0.00	0.00	0.11	0.04	0.38	0
MA1a	P	1	0.24	0.64	0.00	0.00	0.02	0.10	0.04	0.39	0
MA1a	Q	1	0.24	0.68	0.00	0.00	0.00	0.11	0.04	0.46	0
MA1a	R	1	0.16	0.65	0.00	0.00	0.01	0.12	0.05	0.42	0
MA1a	S	1	0.18	0.65	0.00	0.00	0.00	0.11	0.05	0.38	0
MA1a	T	1	0.18	0.53	0.00	0.00	0.00	0.09	0.04	0.31	0
MA1a	U	2	0.96	0.10	0.00	0.00	0.03	0.05	0.03	0.00	1
MA1a	V	1	0.20	0.64	0.00	0.00	0.01	0.11	0.04	0.38	0
MA1a	X	1	0.19	0.63	0.00	0.00	0.00	0.11	0.05	0.43	0
MA1a	Y	1	0.21	0.66	0.00	0.00	0.00	0.12	0.04	0.39	0
MA1a	Z	1	0.21	0.73	0.00	0.00	0.00	0.12	0.05	0.48	0
MA1a	AE	3	0.89	0.22	0.09	0.00	0.03	0.05	0.16	0.00	1
MA1a	J	4	1.39	0.18	0.00	0.00	0.03	0.05	0.36	0.00	1
MA1a	&	5	0.51	0.45	0.00	0.00	0.00	0.04	0.07	0.00	1
MA1b	a	5	0.45	0.45	0.00	0.00	0.00	0.04	0.07	0.00	0
MA1b	b	5	0.42	0.48	0.00	0.00	0.00	0.04	0.07	0.00	0
MA1b	c	5	0.42	0.43	0.00	0.00	0.00	0.04	0.08	0.00	0
MA1b	d	5	0.51	0.47	0.00	0.00	0.00	0.05	0.07	0.00	0
MA1b	e	5	0.49	0.46	0.00	0.00	0.00	0.04	0.07	0.00	0
MA1b	f	5	0.47	0.46	0.00	0.00	0.01	0.05	0.07	0.00	0
MA1b	g	5	0.57	0.51	0.00	0.00	0.00	0.05	0.07	0.00	0
MA1b	h	5	0.37	0.41	0.00	0.00	0.00	0.04	0.07	0.00	0

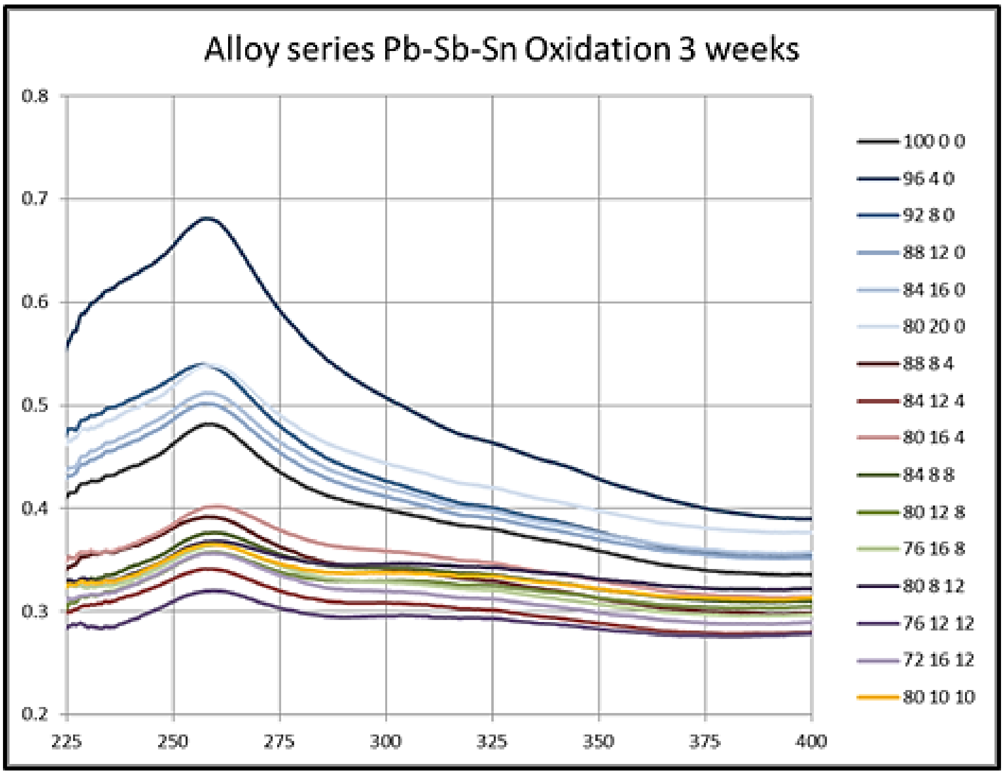
MA1b	i	5	0.41	0.42	0.00	0.00	0.00	0.04	0.07	0.00	0
MA1b	l	5	0.46	0.42	0.00	0.00	0.00	0.04	0.07	0.00	0
MA1b	m	5	0.40	0.44	0.00	0.00	0.00	0.05	0.07	0.00	0
MA1b	n	5	0.46	0.46	0.00	0.00	0.00	0.04	0.07	0.00	0
MA1b	o	5	0.50	0.48	0.00	0.00	0.00	0.05	0.07	0.00	0
MA1b	p	5	0.31	0.34	0.00	0.00	0.02	0.03	0.08	0.00	0
MA1b	q	5	0.43	0.42	0.00	0.00	0.00	0.04	0.07	0.00	0
MA1b	r	5	0.37	0.42	0.00	0.00	0.00	0.04	0.07	0.00	0
MA1b	/	5	0.42	0.42	0.00	0.00	0.00	0.04	0.07	0.00	0
MA1b	t	5	0.41	0.44	0.00	0.00	0.00	0.04	0.08	0.00	0
MA1b	u	3	0.38	0.27	0.00	0.00	0.00	0.02	0.09	0.00	0
MA1b	v	5	0.62	0.46	0.00	0.00	0.00	0.04	0.08	0.00	0
MA1b	x	5	0.48	0.42	0.00	0.00	0.00	0.04	0.08	0.00	0
MA1b	y	5	0.51	0.46	0.00	0.00	0.00	0.05	0.07	0.00	0
MA1b	z	5	0.42	0.43	0.00	0.00	0.00	0.05	0.07	0.00	0
MA1b	s	5	0.52	0.43	0.00	0.00	0.00	0.04	0.07	0.00	0
MA1b	Et	5	0.38	0.37	0.00	0.00	0.00	0.04	0.08	0.00	0
MA1b	oe	4	1.57	0.23	0.00	0.00	0.00	0.04	0.38	0.00	1
MA1b	fi	5	0.50	0.46	0.00	0.00	0.00	0.04	0.08	0.00	0
MA1b	ff	5	0.42	0.41	0.00	0.00	0.00	0.04	0.07	0.00	0
MA1b	/i	5	0.43	0.45	0.00	0.00	0.00	0.04	0.08	0.00	0
MA1b	//	5	0.40	0.35	0.00	0.00	0.00	0.04	0.08	0.00	0
MA1b	/t	5	0.41	0.40	0.00	0.00	0.00	0.04	0.08	0.00	0
MA1b	á	5	0.44	0.42	0.00	0.00	0.00	0.04	0.08	0.00	0
MA1b	à	5	0.38	0.43	0.00	0.00	0.00	0.04	0.08	0.00	0
MA1b	â	5	0.48	0.44	0.00	0.00	0.00	0.04	0.08	0.00	0
MA1b	ã	5	0.45	0.47	0.00	0.00	0.00	0.05	0.07	0.00	0
MA1b	é	5	0.40	0.38	0.00	0.00	0.01	0.04	0.08	0.00	0
MA1b	è	5	0.50	0.53	0.00	0.00	0.00	0.04	0.07	0.00	0
MA1b	ê	5	0.57	0.46	0.00	0.00	0.00	0.04	0.08	0.00	0
MA1b	~e	5	0.52	0.51	0.00	0.00	0.00	0.05	0.06	0.00	0
MA1b	e5	5	0.48	0.47	0.00	0.00	0.00	0.05	0.07	0.00	0
MA1b	~r	5	0.44	0.46	0.00	0.00	0.00	0.04	0.07	0.00	0
MA1b	í	5	0.40	0.41	0.00	0.00	0.00	0.03	0.07	0.00	0
MA1b	ì	5	0.43	0.44	0.00	0.00	0.00	0.04	0.08	0.00	0
MA1b	î	5	0.33	0.37	0.00	0.00	0.00	0.03	0.08	0.00	0
MA1b	~i	5	0.36	0.39	0.00	0.00	0.00	0.04	0.08	0.00	0
MA1b	ó	5	0.41	0.40	0.00	0.00	0.00	0.04	0.07	0.00	0
MA1b	ò	5	0.35	0.39	0.00	0.00	0.00	0.04	0.07	0.00	0
MA1b	ô	5	0.37	0.39	0.00	0.00	0.01	0.04	0.07	0.00	0
MA1b	õ	5	0.40	0.40	0.00	0.00	0.00	0.04	0.08	0.00	0
MA1b	~p	5	0.35	0.37	0.00	0.00	0.00	0.04	0.08	0.00	0
MA1b	~q	5	0.39	0.38	0.00	0.00	0.00	0.04	0.08	0.00	0
MA1b	ú	5	0.53	0.54	0.00	0.00	0.01	0.05	0.07	0.00	0
MA1b	ù	3	0.37	0.34	0.00	0.00	0.00	0.04	0.08	0.00	0

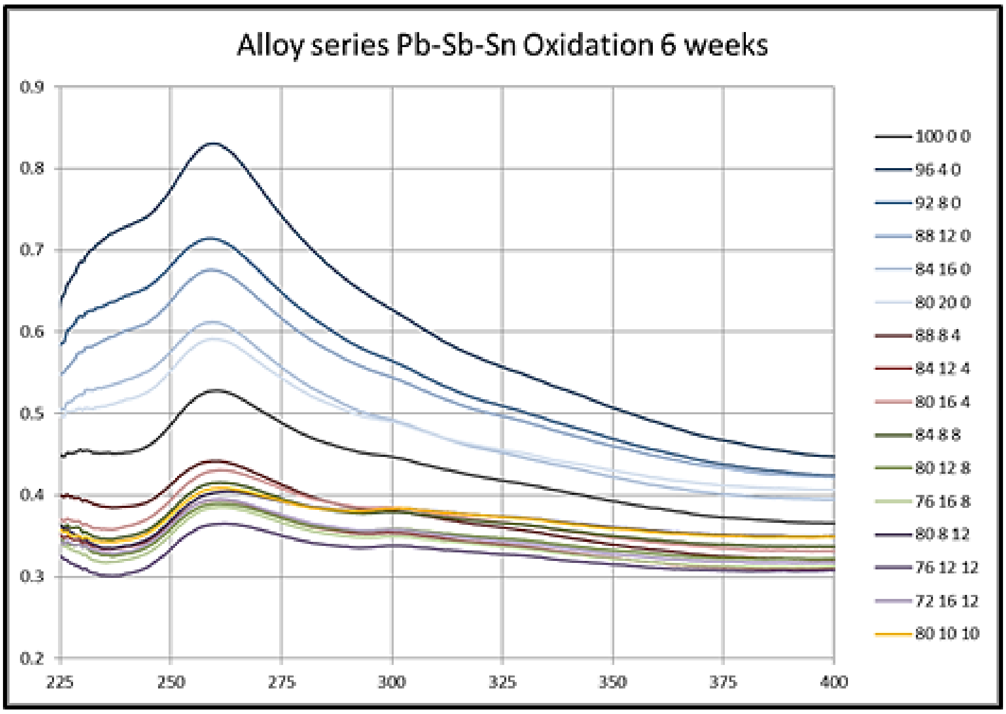
MA1b	û	5	0.43	0.43	0.00	0.00	0.01	0.05	0.08	0.00	0
MA1b	~u	5	0.43	0.43	0.00	0.00	0.00	0.04	0.07	0.00	0
MA1b	ñ	5	0.49	0.41	0.00	0.00	0.01	0.04	0.08	0.00	0
MA1b	j	6	0.52	0.00	0.00	0.00	0.00	0.13	0.00	0.00	1
MA1b	ae	4	1.25	0.21	0.00	0.00	0.01	0.05	0.37	0.00	1
MA1b	k'	2	0.39	0.26	0.00	0.00	0.00	0.08	0.18	0.00	0
MA1b	*	6	0.53	0.00	0.00	0.00	0.00	0.13	0.00	0.00	0
MA1b	qg	2	0.02	0.00	0.00	0.00	0.06	0.08	0.09	0.00	1
MA1b	?	5	0.39	0.40	0.00	0.00	0.00	0.03	0.08	0.00	0
MA1b	'	1	0.31	0.72	0.00	0.00	0.03	0.12	0.03	0.45	0
MA1b	;	5	0.45	0.43	0.00	0.00	0.00	0.04	0.08	0.00	0
MA1b	,"	5	0.44	0.44	0.00	0.00	0.00	0.04	0.07	0.00	0
MA1b	.	5	0.44	0.42	0.00	0.00	0.02	0.04	0.08	0.00	0
MA1b	:	5	0.45	0.43	0.00	0.00	0.00	0.05	0.07	0.00	0
MA1b	´	1	0.32	0.70	0.00	0.00	0.03	0.11	0.04	0.41	0
MA1b	^	1	0.43	0.70	0.00	0.00	0.04	0.12	0.04	0.41	0
MA1b	(	5	0.92	0.56	0.00	0.00	0.00	0.04	0.09	0.00	1
MA1b	-	6	0.29	0.00	0.00	0.00	0.02	0.12	0.02	0.00	1
MA2	A	2	0.09	0.00	0.00	0.00	0.06	0.03	0.11	0.00	0
MA2	B	2	0.38	0.00	0.04	0.00	0.17	0.05	0.12	0.00	0
MA2	C	2	0.07	0.00	0.00	0.00	0.06	0.05	0.11	0.00	0
MA2	D	2	0.06	0.00	0.00	0.00	0.13	0.06	0.12	0.00	0
MA2	E	2	0.07	0.00	0.00	0.00	0.11	0.05	0.11	0.00	0
MA2	F	2	0.08	0.00	0.00	0.00	0.09	0.06	0.12	0.00	0
MA2	G	2	0.10	0.00	0.00	0.00	0.19	0.08	0.08	0.00	0
MA2	H	2	0.13	0.00	0.00	0.00	0.23	0.08	0.07	0.00	0
MA2	I	5	1.01	0.56	0.00	0.00	0.04	0.03	0.09	0.00	1
MA2	K	2	0.17	0.00	0.00	0.00	0.10	0.05	0.11	0.00	0
MA2	L	2	0.17	0.00	0.00	0.00	0.15	0.08	0.07	0.00	0
MA2	M	2	0.30	0.00	0.00	0.00	0.10	0.06	0.10	0.00	0
MA2	M1EAR	2	0.31	0.00	0.00	0.00	0.23	0.08	0.08	0.00	0
MA2	N	7	0.36	0.00	0.00	0.00	0.62	0.07	0.11	0.00	0
MA2	O	2	0.20	0.00	0.00	0.00	0.20	0.08	0.08	0.00	0
MA2	P	2	0.23	0.00	0.00	0.00	0.16	0.06	0.11	0.00	0
MA2	Q	2	0.21	0.00	0.00	0.00	0.15	0.06	0.11	0.00	0
Full list digitally available from the author (8864 entries)											

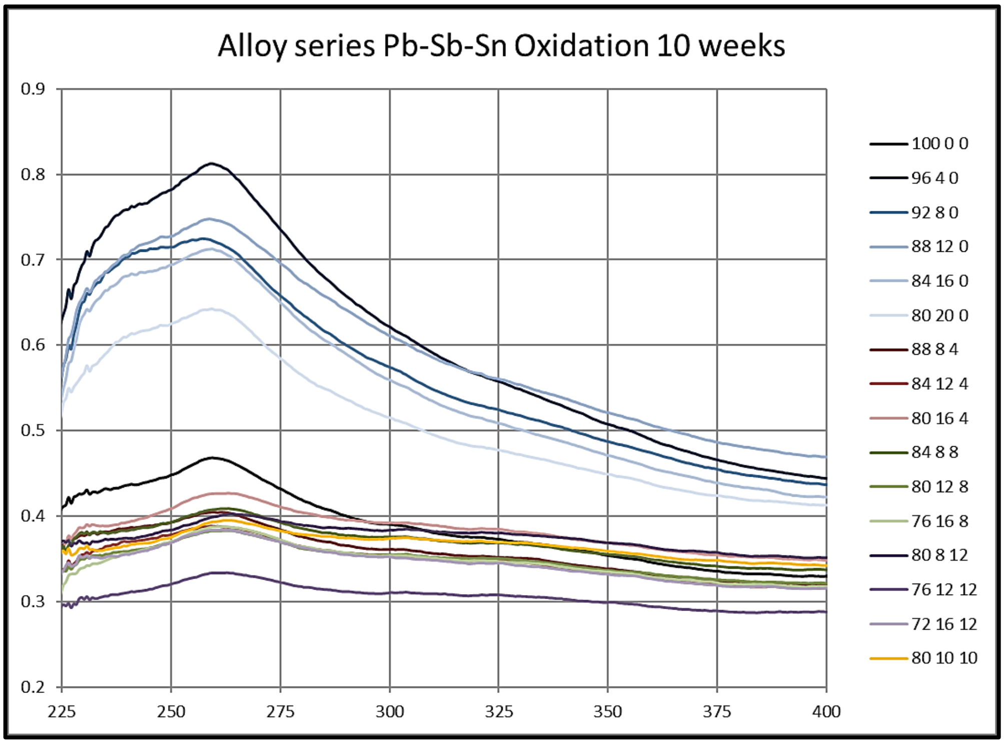
10 Chapter 6: Spectra of UV-Vis measurements

Ambient air oxidation spectra after 1, 3, 6 and 10 weeks of ageing:






Alloy series Pb-Sb-Sn Oxidation 6 weeks
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
225
250
275
300
325
350
375
400
100 0 0
96 4 0
92 8 0
88 12 0
84 16 0
80 20 0
88 8 4
84 12 4
80 16 4
84 8 8
80 12 8
76 16 8
80 8 12
76 12 12
72 16 12
80 10 10


Alloy series Pb-Sb-Sn Oxidation 10 weeks
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
225
250
275
300
325
350
375
400
100 0 0
96 4 0
92 8 0
88 12 0
84 16 0
80 20 0
88 8 4
84 12 4
80 16 4
84 8 8
80 12 8
76 16 8
80 8 12
76 12 12
72 16 12
80 10 10

11 Photographs of the boxes with matrices at the MPM

A digital folder is available on request from the author or at the museum Plantin-Moretus.

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