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Abstract

Electrotyping processes have received considerable attention from the beginning of its invention in 1838. This new technique has been immediately implemented not only in various fields of industry but also very successfully in diverse fields of arts and graphics, particularly for their reproduction. The early application of electrochemical deposition was primarily due to the excellent mechanical properties of plated copper and the new ability to perfectly copy and multiply objects. In addition, non-conductive materials could be coated.

The present physico-chemical study endeavoured the elucidation of the historical objects' composition and the manufacturing processes applied in the 1840s. This basic interdisciplinary research in a historical context focussed on the art-historical and technical processing of metal objects in a recently descovered collection of the Technisches Museum Wien. It was based on systematic material analyses of more than 70 original objects from the first Austrian laboratory for electroplating. Application-oriented conservation-scientific investigations were carried out, as well as electrochemical cleaning methods were developed. New knowledge about the technical implementation as well as the pioneering authors' contribution to the further development of electroplating and photography in Austria, and beyond, was achieved in this work.

One of the central topics of electrochemical deposition on non-conductive substrates is the choice of the conductive layer. It was shown experimentally that graphite powder, as a conductive phase, is superior to silver and copper powder. The material properties of the electrodeposited copper, but also the use of various post-treatment processes, such as compaction by various polishing processes and/or organic and inorganic coating residues on the surface, have a long-term effect on the durability and corrosion behaviour.

The first worldwide-known etched daguerreotype, a heliogravure on silver-plated copper, intended for reproduction by printing was discovered among the electrotype plates from Theyer's laboratory. The breakthrough photographic technique developed in Vienna provided a hitherto unachieved high photosensitivity in contrast to the technology of the French inventor of photography, Daguerre, due to the application of halogenide mixtures without the development with Hg. Surface analyses showed that the photographic process led to the formation of colloidal Ag nanoparticles (AgNPs) with sizes of 30-120nm with shell layers consisting of Ag_2O, Ag_2S, and some AgCl. The image development consisted in the reduction

of the Ag halides to AgNPs adjacent to the latent image Ag nuclei by H_2SO_3. The image was fixed either by KCN or $Na_2S_2O_3$. The investigated plate exhibits etched areas with Ag_2O conversion layers, but no Cl, S, and Hg. This finding showed that the Viennese photographic process of the 1840s contrasted to the French invention by Daguerre in 1839 insofar that it enabled a high sensitivity for moving scenes and the first possibility for reproduction. This triggered the route to the development of modern analogue photography.

Kurzfassung

Die Galvanotechnik hat seit Beginn ihrer Erfindung im Jahr 1838 große Aufmerksamkeit erregt. Diese neue Technik wurde nicht nur in verschiedenen Industriezweigen sofort umgesetzt, sondern auch sehr erfolgreich in verschiedenen Bereichen der Kunst und Grafik, insbesondere bei der Reproduktion. Die frühe Anwendung der elektrochemischen Abscheidung war vor allem auf die hervorragenden mechanischen Eigenschaften von plattiertem Kupfer und die neue Möglichkeit, Objekte perfekt zu kopieren und zu vervielfältigen, zurückzuführen. Darüber hinaus können auch nichtleitende Materialien beschichtet werden.

Die vorliegende physikalisch-chemische Studie beschäftigte sich mit der Aufklärung der Zusammensetzung der historischen Objekte und der in den 1840er Jahren angewandten Herstellungsverfahren. Diese interdisziplinäre Grundlagenforschung im historischen Kontext konzentrierte sich auf die kunsthistorische und technische Bearbeitung von Metallobjekten in einer kürzlich entdeckten Sammlung des Technischen Museums Wien. Sie basierte auf systematischen Materialanalysen von mehr als 70 Originalobjekten aus dem ersten österreichischen Laboratorium für Galvanotechnik. Anwendungsorientierte konservierungswissenschaftliche Untersuchungen wurden durchgeführt und elektrochemische Reinigungsverfahren entwickelt. Neue Erkenntnisse über die technische Umsetzung sowie der bahnbrechende Beitrag der Wiener Autoren zur Weiterentwicklung der Galvanik und Fotographie in Österreich und darüber hinaus wurden in dieser Arbeit gewonnen.

Eines der zentralen Themen der elektrochemischen Abscheidung auf nichtleitenden Substraten ist die Wahl der leitenden Schicht. Experimentell wurde gezeigt, dass Graphitpulver als leitfähige Phase Silber- und Kupferpulver überlegen ist. Die Materialeigenschaften des galvanisch abgeschiedenen Kupfers, aber auch der Einsatz verschiedener Nachbehandlungsverfahren, wie z.B. Verdichtung durch verschiedene Polierverfahren und/oder organische und anorganische Beschichtungsreste auf der Oberfläche, haben einen langfristigen Einfluss auf die Beständigkeit und das Korrosionsverhalten.

Die erste weltweit bekannte geätzte Daguerreotypie, eine Heliogravure auf versilbertem Kupfer, die zur Reproduktion durch Druck bestimmt war, wurde unter den Druckplatten aus Theyers Laboratorium entdeckt. Die in Wien entwickelte bahnbrechende Fototechnik ermöglichte eine bisher unerreicht hohe Lichtempfindlichkeit im Gegensatz zur Technologie des

französischen Erfinders der Fotografie, Daguerre, durch die Anwendung von Halogenidmischungen ohne einen Entwicklungsprozeßschritt mit Hg. Oberflächenanalysen zeigten, dass der fotografische Prozess zur Bildung von kolloidalen Ag-Nanopartikeln (AgNPs) mit einer Größe von 30-120 nm führte, deren Außenschichten aus Ag_2O, Ag_2S und etwas AgCl bestehen. Die Bildentwicklung bestand in der Reduktion der Ag-Halogenide zu AgNPs angrenzend an die Ag-Keime des latenten Bildes durch H_2SO_3, das entweder durch KCN oder $Na_2S_2O_3$ fixiert wurde. Die untersuchte Platte weist geätzte Bereiche mit Ag_2O-Konversionsschichten auf, aber kein Cl, S und Hg. Dieser Befund zeigte, dass der Wiener Fotoprozess der 1840er Jahre im Gegensatz zur französischen Erfindung von Daguerre von 1839 stand, da er eine hohe Empfindlichkeit für bewegte Szenen und die erste Möglichkeit der Reproduktion ermöglichte. Dies war der Auslöser für die Entwicklung der modernen Analogfotografie.

Preface

In recent years, I tried to put together a complex puzzle of an almost forgotten and little-known aspect of Austrian technological history. The research of the only known legacy of the first Austrian laboratory for electroplating technology led us to the topics of graphic prints, reproduction processes and, surprisingly, into the very early history of photography in Austria. Both topics are of incredible complexity and after about 160 years it is almost impossible to reconstruct all aspects comprehensibly. Nevertheless, many pieces of the puzzle could be identified and put in the right order. Some fragments remain hidden, leave gaps in knowledge and need further research. But the most important fact is that some main aspects of the manufacturing processes and the technological development of electroplating and early photography have been identified and published.

At this point I would like to express my most sincere thanks to Professor Dr. Wolfgang Kautek. Only through his help and great support, but also his belief in this unconventional scientific work on the Austrian technological history, it was possible to bring this study to a round final.

The transfer from the University of Applied Arts to the Department of Physical Chemistry of the University of Vienna was both a challenge and an incredible enrichment. The confrontation with a different approach to research and publishing has often pushed me to my limits. All this time, the boundless trust and support of my dear family has been my driving force. Thank you, my husband Wolfgang, my daughter Nina, and Mama.

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1. Introduction and motivation

Cultural heritage is the key element of each nation's cultural identity. Restoration and conservation as a discipline and profession is directly involved in the preservation of this heritage for future generations. Conservation and preservation measures are only possible if we are well acquainted with historical production methods in materials technology, if we understand and link age-related changes and characteristics with the historical use and individual history of the object. Very often we have no such information and know nothing about the objects and their history. At this point, scientific research is enormously valuable. It supports conservators with facts and plays a decisive role in finding solutions for individual conservation problems, in the development of special conservation techniques and in disaster management and preventive conservation. Therefore, the interdisciplinary exchange of knowledge between the three main areas - natural sciences, history of art and technology, and nature conservation - is so important.

The Technisches Museum Wien (TMW) is one of the six largest museums in Austria and holds an enormous number of objects, whose origin sometimes requires extensive research. Even today, such historical collections contain valuable new findings for the further development of technology and science. Their material-technological research is also of substantial importance for conservation science and further preservation in a museum environment. Such collections can be adequately preserved for the future when they are based on profound knowledge of their material properties and historical manufacturing processes.

A very rare and unusual group of objects came to our attention – the first metal objects produced by electrochemical deposition in Austria. Items from the earliest period of electroplating technology are a peculiarity and represent a knowledge base of this still today industrially irreplaceable technology. Another special feature of these objects is that they were used for the printing of art graphics in a time in which there were no clearly regulated print runs and almost no restrictions on the reproduction of graphic art. With the development of electroplating, the boundary between the original and the copy disappeared almost completely. It is therefore extremely difficult to identify graphics and graphic techniques from the middle of the 19th century, since electrochemical deposition made it possible to reproduce printing plates faithfully to the original and without restriction, regardless of the technique used to produce the originals.

1.1. Problem complexes

Electrotype artefacts from the earliest period of electrotyping are rare and can be regarded as a base for modern industrial manufacturing technology [1,2]. Electrotyping processes have received considerable attention at the beginning of its invention in the early 1840s [3]. This new technique has been immediately implemented not only in various fields of industry but also, very successfully, in diverse fields of arts and graphics, particularly for their reproduction [4–7]. However, our knowledge concerning the production of early electrotype artefacts for graphic arts is very limited. Solely, general information can be found in early publications [8–14] and technical encyclopedia from the 19th century [5,12,15–17]. Since then, little scientific work about the used materials and techniques has been undertaken in detail.

The subject of the following work is the scientific examination of early, electrotyped printing plates from the Laboratory of Franz Theyer and Erwin Waidele, who worked in Vienna at the beginning of the 1840s [8,18–35]. Theyer's last known legacy is part of the collection of the Technisches Museum Wien (TMW) and includes approximately 70 historic documents, 217 graphic prints as well as 76 copper printing plates and small silver and gold-plated medallions. The extraordinary mixture of different objects caught our attention during the inventory in 2008. The subject at hand is a drawer cabinet labelled "Galvanoplastik und deren Anwendung. Franz Theyer, Wien 1839-1851" ("Galvanoplasty and its application. Franz Theyer, Wien 1839-1851"). According to information from the k.k. Technologisches Gewerbe-Museums (TGM), this group of objects was donated by Theodor Theyer, the son of Franz Theyer, in 1889 [36]. The collection was taken over by the TMW at its foundation in 1909. Due to a lack of written sources from the founding period of the TMW, it has not yet been possible to ascertain whether these early objects were exhibited in the museum's first show collection.

The collection from the laboratory of Franz Seraphin Theyer (1809 - 1871) and Erwin Waidele introduces an interesting topic - both historically and technically speaking – a combination of the electrotyping technique with graphic art and photography. These two techniques were discovered and developed simultaneously at the end of the 1830s. They both reached Vienna from Russia [37] and France [38–40] in 1839, where they were further developed. People involved in the first phase of experimental scientific research in the fields of electrotyping and photography in Vienna belonged to the same circle [41]. They were not

only interested in the technical advances that accompanied new inventions but also in the promotion of their further development [41,42]. This search for new methods of reproduction was fuelled by the desire to make graphic art accessible to a wider range of people [6,7,43,44].

1.2. Aims and objectives

This work comprises the first inventory of the 73 original metal objects and a large number of documents (20 excerpts from newspapers, magazines and brochures, over 50 letters, directories and other handwritten documents as well as over 200 test prints) from the "Franz Theyer's galvanoplastisch-artistischen Laboratorium". Another three original plates from the same manufacturer were found in the collection of the TMW and assigned to the same workshop. According to the inscription on the wooden cabinet [8,18–35] the objects were manufactured between 1839 and 1851. This time was verified and corrected in the course of the work. At the beginning of present study, all objects were briefly recorded in written and photographic form in the TMW database (Appendix). Further processing of the original written material also includes the transcription of all original documents from the Theyer’s estate. This is intended to provide a more detailed historical classification of the data and a better understanding of the achievements of Theyer and E. Waidele.

The questions and issues resulting from observations made during this study can mainly be ascribed to a scarcity of information about the production processes, the chemical and morphological composition of the plates and their differing corrosion properties. The scientific research is therefore based on a systematic analysis of material on the objects using various bulk and surface methods. The development of cleaning, storage and exhibition concepts that are acceptable regarding their preservation and conservation requires knowledge of the material and the manufacturing technique of the object, on the one hand, and chemical and physical knowledge of organic and inorganic substances on the surface, on the other hand, as well as the associated material aging and corrosion processes. Application-oriented basic examinations promise to provide a clearer methodology for the identification of the techniques employed and respective deterioration phenomena, and thus facilitate focussed conservation and restoration measures. Great importance will be attached to the use of non-destructive methods [45–47].

In order to gain a better understanding of all relevant processes for the historically described methods of early electroplating, concrete experiments were carried out in the field of metal deposition on conductive and non-conductive surfaces. The aim was to learn more about the material properties, conductive layers and their behaviour during moulding and reproduction of printing plates, and more specifically about the technique of galvanography.

2. Outline of the techniques, history and the artefacts

2.1. Overview of graphic techniques and prints

The term "graphics" refers to the collective definition of all activities of graphic image design, but also to its manual printing and duplication [43]. The art of manual image printing is strictly defined as the transfer of ink/dye from a printing surface to a sheet of paper or another material [6,43]. We distinguish four main groups of prints: intaglio, relief, planographic and through-printing (porous). The total number of prints is called "edition" and is usually limited by the artist. The limitation of the editions was introduced around 1880 in order to protect the buyers as well as the artists, and to prevent the inferior quality of the prints and their unlimited reproduction [43].

Copper engraving is the oldest graphic intaglio printing process in which depressions are dug into the copper plate [6,43,48,49]. The word copper engraving is often used as a generic term for all graphic techniques. The basic engraving is a line engraving created with a burin. The print on paper made with an engraved copper plate is also called copper engraving. Since their first application by goldsmiths, probably in the 12th century, numerous other methods and tools, as well as chemical processes, have been developed for treating the copper surface besides the original burin engraving [48,50,51]. Fig. 1 gives an overview of the eleven most common processing methods:

1. Line stitch
2. Drypoint etching
3. Etching
4. Aquatint
5. Mezzotint
6. Punching stitch
7. Point stitch
8. Soft ground etching
9. Dottier manner
10. Roulette technique
11. Crayon manner

These are often not distinguishable by the naked eye and can only be determined by a strong magnification [6].

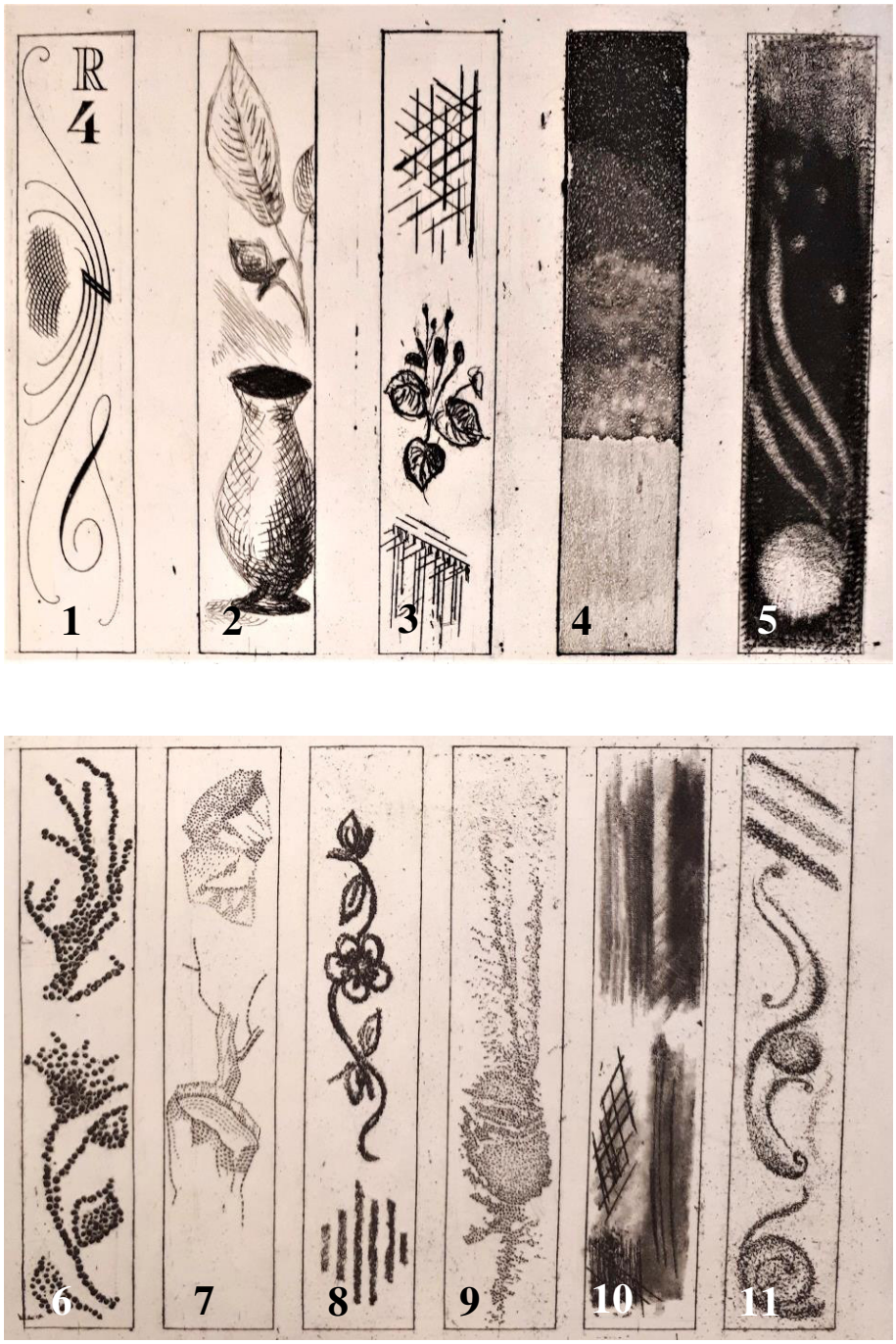

Fig. 1 Eleven techniques on one plate by Georg Wimmer, Vienna 1964

2.2. Galvanoplasty and Electrotyping

2.2.1. Terms and terminologies

The technique of galvanoplasty or electrotyping was discovered by Moritz Hermann von Jacobi in St. Petersburg in 1838 (Fig. 2) [1,2,37]. While electroplating is a process in which the surface of a metal object is coated with a layer of another (noble) metal by electrochemical deposition, the electrotype is an item produced by electroplating a mould [10,12,13,52–55]. The process of the surface electroplating is a short one, since the layer thickness does not have to be great. Electrotyping requires much more time until the thickness of the deposited material can withstand a certain mechanical load, such as with printing plates.

Not only metallic objects could be refined with a metal coating, but other materials such as plaster, wood, leaves, flowers and animals could also be electrolytically coated with a metal layer [13,16,26,54,56,57]. The materials, which did not conduct the electric current themselves, firstly had to be provided with a conductive coating (e.g. graphite or metal powder).

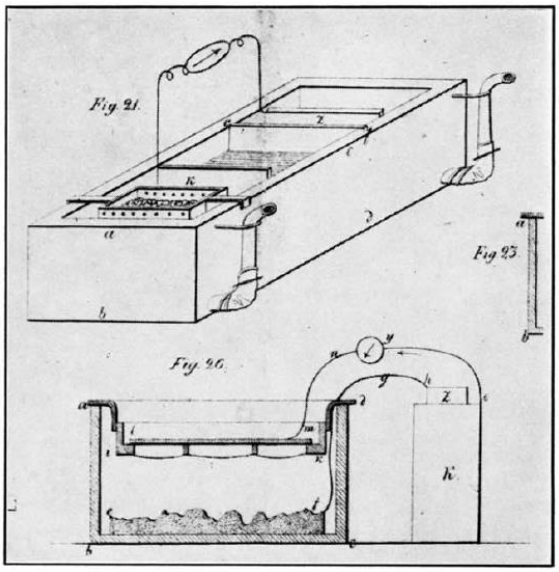

Fig. 2 Two types of apparatus used by Jacobi, aus “Die Galvanoplastik” von M.H. von Jacobi

2.2.2. Galvanography

Copper could be deposited electrolytically on non-conductive materials which had been pre-treated with conductive layers (e.g. graphite), as Kobell [58,59] had already observed in Munich in 1839. Thus, he succeeded to accurately copy painted copper plates in the galvanic bath. Theyer and Waidele further developed Kobell's painting medium to improve image production and transfer quality. They called it Elekrotinte [9]. The painting medium had to adhere to the plate and be endure the galvanic bath. The painting media contained mixtures of ferric oxide, ochre, graphite, vine black with wax, which were dissolved in terpentine oil or dammar varnish and were applied onto the silver-coated copper plates. The thick pasty layers of paint had to be made conductive by adding graphite, whilst the thin layers did not require this additive [33,36,54]. There is also written evidence that silver powder was included in the mixture on occasions to improve conductivity [13,16,59].

Silver played an important role as a separation layer in the production of galvanographies. Initially, the original plates were coated with a thin layer of oil or grease to enable the newly formed galvanic copy to be separated from the original [60]. However, it was almost impossible to spread the grease coat equally thinly over all heights and depths. This had an effect on the originality of the replica, and the fine structures lost their sharp outlines. Kobell proposed a solution that was adopted by other workshops. He placed the original plates in a dissolution of chloride silver and table salt for about 10 minutes before taking the galvanic impression. The outermost copper atoms were displaced from the surface by the silver atoms. This thin Ag film served as a separating layer and had no visible influence on the surface morphology [60].

Once the galvanic copper layer had attained a sufficient thickness, the electrochemical process was stopped. The deposited negative mould could be delaminated mechanically from the positive substrate after the rims of the multilayer composite were removed. The edges and corners of the detached mould were further rounded with a file. The rear side that had been in contact with the electrolyte always had a rough surface which was often then smoothed with a file (Fig. 3).

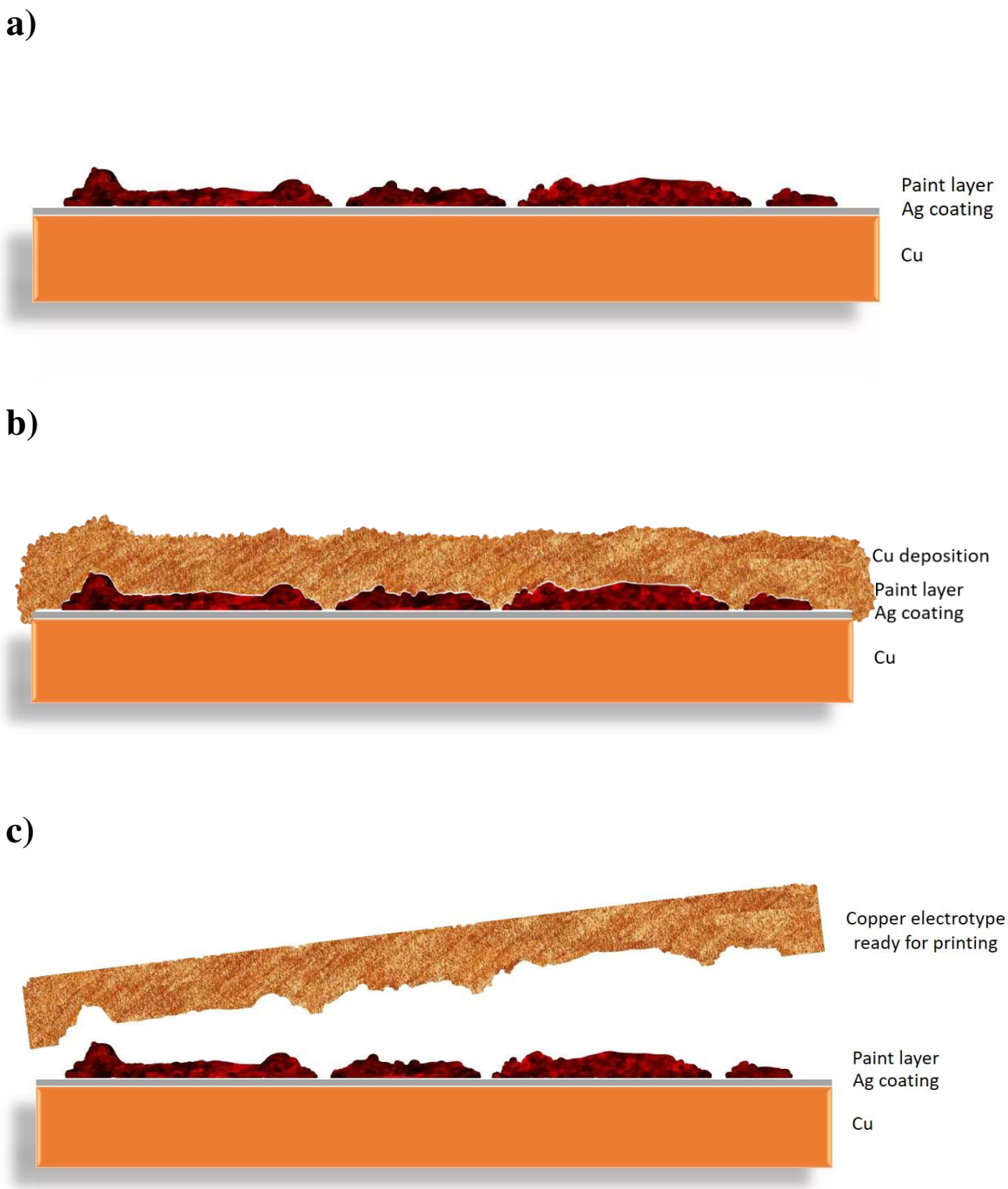

Fig. 3 The manufacturing steps in the production of electrotypes

This study is not only intended to provide a conservation methodology for the treatment of electrotype printing plates but also an aid in the identification and classification of the plates themselves. Furthermore, this will hopefully assist paper conservators with a more reliable system to identify prints produced during the 1840s, a period of great experimental innovation which has yet to be more fully researched (Fig. 4).

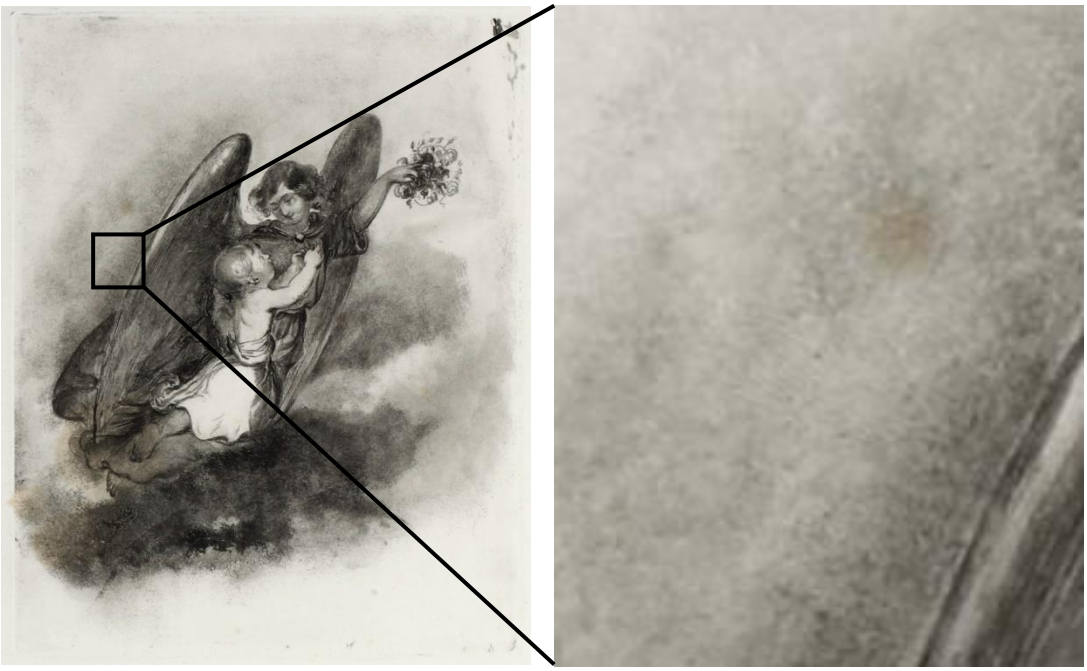

Fig. **4** Left: Galvanograph print on paper. Right: fingerprints on the left side of the angel's wing. BPA-015561-03, © TMW Archiv.

2.3. The early application of electrotyping and galvanography in Vienna

In 1839, the Niederösterreichischer Gewerbeverein (Lower Austrian Trade Association) was established in Vienna. The members – factory owners, tradesman and people interested in scientific innovation – were concerned with current inventions and searched for ways of commercial implementation. Among other things this included the daguerreotype process as well as a series of methods employing electrochemical reactions using batteries. Several businessmen in Western Europe applied the coating process on objects in an electrochemical manner with precious metals and consequently left traditional processes such as fire gilding [61] and silver plating behind. Those coating techniques targeting to permanently combine two metals were described as electroplating [5,10,12,13,15,52,53]. The electroforming method was based on the same electrochemical principles but served a different purpose: the surface of a negative mould was coated with a copper electrotype layer. The mould and its electrotype layer were removed from the solution, and the electrotype positive was detached.

The early application of electrotyping to produce printing plates and other objects was primarily due to the excellent mechanical properties of electrolytically deposited copper and a newly perfected ability to copy and reproduce objects. The Viennese businessman Franz Theyer [62] also experimented with different forms of electrotyping [8,22,23,25–27,30,32–35,63–73]. Theyer's main concerns were the production of high-quality glossy plates for engravers, the manufacture of copies of engraved plates as well as galvanography [11,32,33,36,55,57,60,63,74–76]. For the purpose of exact duplication, Theyer experimented using various printing plates, not only copper engravings and dry needle plates but also aquatint plates. The process eventually made it possible to produce a mould to duplicate all of these plates successfully. The original plate was only used a small number of times in order to level out irregularities in the printed image before an electrotype mould was then taken. It was possible to produce any number of electrotype duplicates from a plate and therefore an unlimited number of prints [4].

Due to the high quality of the results the laboratory gained a lot of recognition and sold their electrotyped plates not only to clients at home but also abroad [36,68]. Written records in the form of newspaper articles, bills and letters between Theyer and his business partners do not reveal enough detailed information on the processes tested and employed in the laboratory. His experiments started with galvanography and were expanded to include photography.

Some of the metal objects found in the cabinet, such as galvanographs, electrotyped copper plates, gold and silver-plated medallions, could be vaguely identified. However, a series of objects raised important questions regarding the manufacturing technique and the significance of particular characteristics.

It is still unknown in which year the laboratory closed. The reports about Theyer's activity in the field of electroplating cease in 1845. The Viennese physicist and photographer Anton Martin referred to Franz Theyer studies of photography in a publication on the Austrian contribution to the development of manufacturing and technology. He mentioned Theyer’s laboratory, stating that its ‘active period’ was restricted to the period between 1843 and 1845 [76]. However, the cupboard containing his collection has an inscription with the years 1839 – 1851, but this may be due to the incorrect memory of his son who had this cabinet made [33,36].

3. Methods and Materials

3.1. Experimental methods

A systematic materials analysis of all historic objects has been undertaken (Table 1). The focus of this work was on extensive material-technological investigations of the surface morphology and its chemical composition. Morphological analyses were performed using SEM, Z-scanning optical microscopy. Chemical results were obtained with EDX, XRD, ATR infrared spectroscopy, XRF and LIBS.

Table 1. Implemented diagnostic procedures

Methode	Morphologie	Chemie
Rasterelektronenmikroskopie mit Energiedispersiver Röntgenspektroskopie (REM, EDX)	X	X
Laser-Induced Breakdown Spectroscopy (LIBS)		X
Z – Scanning (Mikroskopie)	X	
Röntgendiffraktometrie (XRD)		X
Attenuated Total Reflection Fourier-Transform Infrared Spectroscopy (ATR-FTIR)		X
Energiedispersive Röntgenfluoreszenz-Spektrometrie (XRF)		X
Electrochemical methods (voltammetrie, electrochemical pencil)		X

3.1.1. Characterization of surface topography and chemical composition

Optical microscopy (Olympus GX51, Happy Plating GmbH) could be complemented by a digital microscope (Keyence, VHX-5000) together with the z-scan techniques. A systematic surface analysis of the original objects was carried out using a scanning electron microscope. Energy dispersive X-ray spectroscopy was performed on the same objects to characterize the element composition. A total of 68 objects were examined using this technique. The investigations had to be carried out at the Vienna Institute for Archaeological Science, University of Vienna (Zeiss EVO 60 XVP) and the University of Applied Arts Vienna when the sample size required a larger sample chamber than was provided at the Faculty Center for Nano Structure Research, University of Vienna (Zeiss Supra 55 VP).

3.1.2. Investigation of coating ticknesses

The thickness of the metal coating on all electrotype objects with silver or gold deposits was investigated using X-ray fluorescence analysis (XRF, Röntgenanalytik Messtechnik GmbH, maXXi 5 PIN, at Happy Plating GmbH).

Additionally, depth profile analyses of thin film layer systems (Cu, Cu-Ag, Cu-Au) were carried out by means of Laser Induced Breakdown Spectroscopy (LIBS) with the aim of developing a less invasive method for the analysis. A simple model consisting of a copper plate which was 2/3 silver plated and 1/3 additionally gold-plated was used (Fig. 5). Due to the low effort required for sample preparation, the extremely fast measurement results for individual laser pulses and the possibility to analyse thin samples and coatings, LIBS is often used in the field of heritage science.

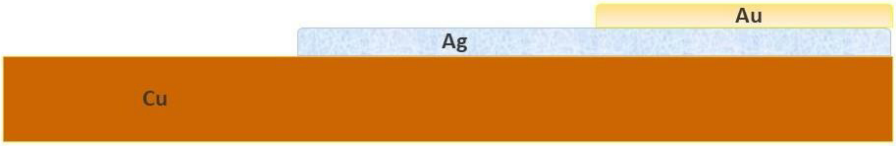

Fig. 5 The used model system

3.2. Use of electrochemical methods in conservation science and practice

Historical objects from the 19th and 20th centuries often exhibit a thin galvanically applied coating, which is largely infiltrated with corrosion products [47,77–82]. They represent a major restauration and conservation problem, as they often cannot be treated with conventional mechanical cleaning methods due to their abrasive effect [83–85]. Electrochemical cleaning methods are characterised by an ideal self-limitation (e.g. complete reduction of an oxide layer) and can be applied locally [84,86–90]. For this reason, electrochemistry formed a focal point of this work, especially with regard to the reduction of silver oxide, and provided new insights into the non-destructive cleaning possibilities of electroplated silver coatings.

In contrast to historical copper alloys, where corrosion layers are a patina worth preserving and an integral component of the object, the silver surface is expected to have a noble and bright metallic appearance. This desired condition can only be maintained by repeated cleaning and removal of corrosion layers. The desired aesthetic idea is the silver, characterized by

usage abrasion and cleaning treatments, but which did not look matt but silky glossy or high-gloss – depending on the function, production time and production method.

The removal of the sulphide layer is always associated with a more or less strong material reduction [91]. The most common silver cleaning method known for centuries is mechanical removal by abrasive media such as pastes or powders. In chemical sulphide removal, silver blackening is reduced by dissolving it in liquids or treating it with gases [79,84,92,93]. Electrochemical cleaning reduces the silver sulphide coating electrochemically to silver.

3.3. Electrochemical metal deposition

3.3.1. Reconstruction of the printing plate manufacturing process by galvanography

For this experiment, 6 equally sized copper plates were cut, their surfaces polished and cleaned (Fig. 6). Four of them were silver plated to determine the behavior patterns of copper and silver during impression taking. The paint was produced with mixtures of burnt umber and vine black pigments, graphite powder, dammar varnish, oil of turpentine, wax and siccative in variable viscosities.

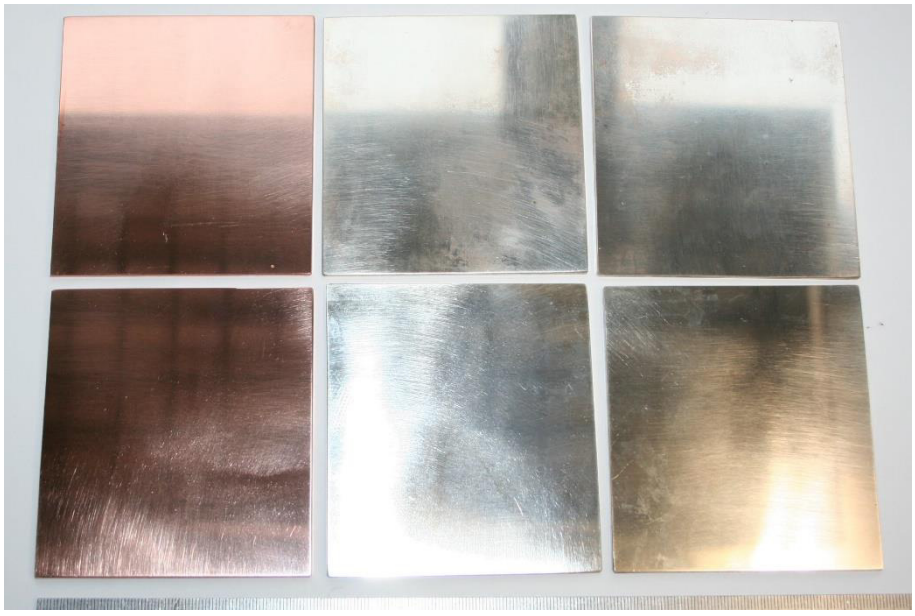

Fig. 6 Copper plate models

3.3.2. Conductive layers

A central aspect of electroplating printing plates is the choice of the conductive layer on the mould. The motif as well as the plate background shall not be affected by the granularity of the conductive layer. The background should appear as smooth and flawless as possible so that the motif is brought to the fore. The production of new electrotype samples and the use of three different conductive coatings – copper powder, graphite and silver powder – were demonstrated. Special attention was also paid to the post-treatment of the finished plates by comparing two different polishing methods with the untreated surface and testing their long-term stability.

4. Publications

List of original publications:

The present doctoral thesis is based on the following publications:

Released publications:

I. Duplication of Uniqueness: Electrotyping in Nature Printing and its Application in Contemporary Art
Valentina Ljubić Tobisch, Albina Selimović, Anna Artaker, Martin Klobassa, Wolfgang Kautek
Heritage Science 7 (2019), DOI: 10.1186/s40494-019-0263-0

II. Highly Photosensitive Daguerreotypes and their Reproduction: Physico-chemical Elucidation of Innovative Processes Developed Around 1840 in Vienna
Valentina Ljubić Tobisch, Wolfgang Kautek
ChemPlusChem (2019), DOI: 10.1002/cplu.201900467

III. Physicochemical characterization of electrodeposited printing plates from the early 1840s in Vienna
Valentina Ljubić Tobisch, Ioana M. Cortea, Lucian Ratoiu, Roxana Rãdvan, Wolfgang Kautek
Microchemical Journal (2019), DOI: 10.1016/j.microc.2019.104320
(In Press)

I. Duplication of Uniqueness: Electrotyping in Nature Printing and its Application in Contemporary Art

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Contributions:
In this paper I was in charge of the conception of the presented idea about conductive layers in electroforming. With the technical support of M. Klobassa the electrochemical precipitation was produced. Together with A. Artaker I also investigated the historical background context, the application and the production process of natural printing. I carried out all investigations at the optical microscope as well as all SEM / EDX investigations. Together with A. Selimović the cyclic voltammetry was carried out. With the support of W. Kautek all data were evaluated, and the manuscript was written.

Keywords: Nature printing, printing plates, electrotyping, conductive layer, heritage science, contemporary art

4.1. Abstract

The nature printing technique was designed for the electrotyping reproduction of leaves and other natural products. Authentic impressions could be performed by inserting leaves between two lead plates or pressing leaves into the lead plate by a press. The impression obtained could then be further reproduced by electroplating. However, this final production step involves decisive differences in the faithfulness of reproductions of original motifs. A central topic in electroforming of printing plates is the choice of the conductive layer on the mould. In the present study, it has been shown that graphite powder represents a conductive phase on the siloxane mould superior to silver and copper powder. The grain size of the copper electrodeposit depended on the powder grain size. The copper plate deposited on graphite powder showed the lowest grain size (5-20 µm) and the highest homogeneity of the print background. Hand polishing of the printing plate resulted in a much better faithfulness of the motif details than that of the machine polished version. However, the background of the print derived from the machine polished plate was the most homogeneous. Electrochemical investigation showed that remnants of the silver powder could result in local elements that could enhance corrosion and thus impair the durability of the printing plates. This phenomenon was negligible with the conductive layers consisting of graphite and copper.

4.2. Introduction

One of the authors, the artist Anna Artaker, presented a series of contemporary nature prints entitled “The Pencil of Nature” at the Bank Austria Kunstforum in Vienna, Austria, in 2017 [94]. She revived the nature printing technique that was developed and patented by Alois Auer and the Austrian National Printing Office (k. k. Hof- und Staatsdruckerei) in 1852 [95]. This technique allowed the production of printing plates from dried plants, fabrics, lace samples, embroideries and other originals. It enabled the production of impressions “identical to the original”, in Auer’s words, both in white colour on dyed ground and in natural colours on white paper, even with the use of delicate embossments and recesses. Two examples are represented in Fig. 7. Neither drawings nor engravings made by human hands were necessary. The main motive for the development and perfection of this printing technique by the Austrian National Printing Office was the possibility of its application in the production of large editions and its interest in duplicating processes.

The main task of this paper is the study and comparison of three conductive layers which have historically been used in the electrochemical deposition of copper. Electrochemical deposition was used fairly quickly after its discovery at the end of the 1830s both for artistic and multiplication purposes [37]. If the matrix material was not electrically conductive, a coating process with an electrically conductive material was necessary. This was achieved either by the application of electrically conductive powders or by electroless metal deposition [14].
The main requirement for the conductive layers is that it generates a thin film imperceptible enough, so that it does not impair the shape or the details of the motifs to be replicated. The cheapest and most commonly used method in historic techniques was graphitizing. Apart from finest graphite powder, metal powders such as silver, copper or even gold powder were used [12,13,15].
The present investigations intended to provide information on the electrical conductivity of graphite, silver and copper powders on the one hand and on the quality and roughness of the electroplated surface on the other hand [96]. The experiments allowed to identify the optimum electrode material for the most ideal moulding and showed whether parts of the conductive layer were transferred to the electroformed positive.

4.3.Methods

4.3.1. The process of Nature Printing – History

A nature print is a print in which an object taken from nature serves as a printing block. They are produced by the direct use of e.g. plants or animal objects – without interaction or artistic interpretation. Nature printing was developed in the Middle Ages to support the collections of medicinal plants in parallel to the botanical tradition of the production of herbaria. The durability of herbaria being limited, botanists started to soak the dried and pressed plants in ink to print them on paper. The first impressions of leaves and fruits obtained were very simple. The earliest dateable nature print dates to 1228. By the 17th and 18th century, nature printing had developed into a serious scientific method of plant reproduction. Nature printing was also popular in Asia, namely in Polynesia, China and Japan, where prints of fish and other sea species are still being produced [97,98].
Historic herbal books describe that both sides of the plant were usually ink-coated [99]. The plant was then placed between two sheets of paper and pressure was applied to achieve a true-to-the-original imprint. This process could be repeated up to two more times without

requiring a renewed soaking of the object in additional ink. Usually six prints could be obtained using the same plant. While the first two prints generally turned out rather dark, the subsequent two prints were the most faithful duplicates. The last two prints often had to be coloured once they had dried out, while the truest second ones were left uncoloured. In the 16th century, several European botanists knew of and applied the technique which was known as *ectypa* or *typographia plantarum* at the time [98,99].

Fig. 7 Left: nature print of spondulicks, 1854, Franz Aspöck, (M. Auer, Faust, Poligraisch-illustrirte Zeitschrift, 1854, Vienna) © Technisches Museum Wien. Right: nature print of Zahlbrucknera, Ettingshausen & Pokorny, k.k. Hof- und Staatsdruckerei, 1856, Vienna, © Technisches Museum Wien

The first step in the process of nature printing, the technique developed by the Austrian National Printing Office 1852, was the creation of an original imprint of the plant in lead by means of a printing press. From this original imprint, a copper intaglio printing plate was produced using the process of galvanoplasty or electrotyping, which was a cutting edge technology at the time [37]. The time-consuming electrotyping process was employed twice. First a positive of the imprinted plant was made from the negative impression in lead [9]. This positive served as a matrix for a second plate produced in a galvanic copper bath, which was

identical to the initial imprint in lead, but suitable as a printing plate. When the quality of the copper printing plate started to deteriorate a new one could be produced from the matrix. In principle, the process enabled a theoretically endless print run, although in practice the laboriousness involved prevented large editions [10,17]. If we consider the touch of the plant that leaves an imprint a unique and irretrievable moment, then the Viennese technique of nature printing enables the paradoxical duplication of uniqueness.

4.3.2. Contemporary attempt to recreate the historic technique

One of the authors, the artist Anna Artaker combines her interest in the history of photography and William Henry Fox Talbot's earliest botanical photograms with a revival of the historical technique of nature printing. If nature is defined as encompassing all phenomena that occur without human intervention, is it possible to reproduce them without changes? While trying to reconstruct the nature printing technique of Alois Auer, questions and problems concerning the surface quality of the produced prints arose. A graininess in the plate background was observed that should appear as smooth and flawless as possible to bring the motif to the foreground. The resulting print exhibits its own base tone originating from the graininess of the matrix (Fig. 8).

Fig. 8 Photographs of the lead plate onto which the plant was impressed (left), of the copper plate, the positive (middle), of the print on paper (right). © Anna Artaker

4.3.3. Electrochemical analysis methods in heritage science

Electrochemical methods of analysis play an increasingly important role in conservation science [86,88]. Particularly advantageous is the fact that they are practically non-destructive methods. In fact, most electrochemical methods of analysis can be performed directly on the object without the necessity of sampling. The size and shape of the object do not play a major role since the electrochemical methods are transportable and can be applied in situ. They can be used to evaluate the protective properties of coatings on metal surfaces in the field of heritage science [100]. Besides the use of electrochemical methods in the analysis of metal objects, the electrolytic reduction of tarnish layers on metals is an established method of intervention in the restoration of metal artefacts [88].

In the present work, cyclic voltammetry was employed to identify the components of the surface layers and their corrosion stability on the produced copper plates as well as the effects of various surface polishing treatments after the electrotyping process.

4.4. Experimental

Production of electrotype samples started with the impressing of plant motives onto a 3 mm thick lead plate. A negative of this plate was produced using a two-component siloxane (MM 240 RTV, Bodo Möller Chemie Austria GmbH) and was mounted on a stable support plate of acrylic glass. One third of the siloxane surface was coated with copper powder (Gold Bronze Powder, Eckart-Werke, Germany), the second third with graphite powder (Graphite Fine Powder extra pure, Merck, Austria) and the last third was coated with silver powder (Silver Powder 1000/1000, Ögussa, Austria). The metal powders exhibited platelet morphologies resulting from their electrolytic production. They were first applied with a soft brush and then smoothed into the siloxane surface with fingers. The excess was removed with compressed air.

The application of the conductive powders were originally carried out with a long-haired brush [14]. The brush was dipped into the conductive powder and led in circular movements over the negative mould until the whole surface showed a metallic shine.

The conductive layers on the siloxane mould were electrically contacted by an insulated copper wire (Fig. 9a). This wire also served as a mechanical suspension device in order to hold the acrylic base and the mould in the electrolytic bath. An additional contact silver lacquer electrode was applied along the circumference of the sample (Fig. 9b). The space between

the acrylic glass plate and the siloxane mould was sealed with liquid wax to prevent the electrolyte from penetrating in between.

This sample was submersed into a sulphuric acid thick-film copper bath (Bright Copper ACG 8, Schlötter Galvanotechnik) at 20°C (Table 2). The producer states that it contains a single additive for brightness and levelling (chemical identity undisclosed). The bath was kept in constant motion by a pump. A DC-power supply (Heraeus, 10V, 100A) served as current source for the electrolysis. The copper anodes (200x400 mm, 1 cm thick) were covered by polypropylene anode bags. A voltage of 0.5 V was applied until the entire sample surface was overgrown. Then, it was increased to 2 V. After four hours, the negative plate (working electrode) was rotated by 180° and the electrolysis was continued another four hours. After this electrodeposition process, the deposited copper plate (Fig. 9c) was separated from the underlying mould with a blunt knife which was inserted between the siloxane negative and the copper positive. The copper plate was rinsed with water and buffed with a soft brass wire brush, as described in the historical reports [12,13,15].

Table 2. Galvanic bath "Glanzkupferbad ACG 8"

Parameter	Information provided by manufacturer
Cu concentration	39,0 gl^{-1}
H_2SO_4 concentration	97,8 gl^{-1}
Cl^- concentration	58,0 g^{-1}
Fe concentration	0,1 gl^{-1}

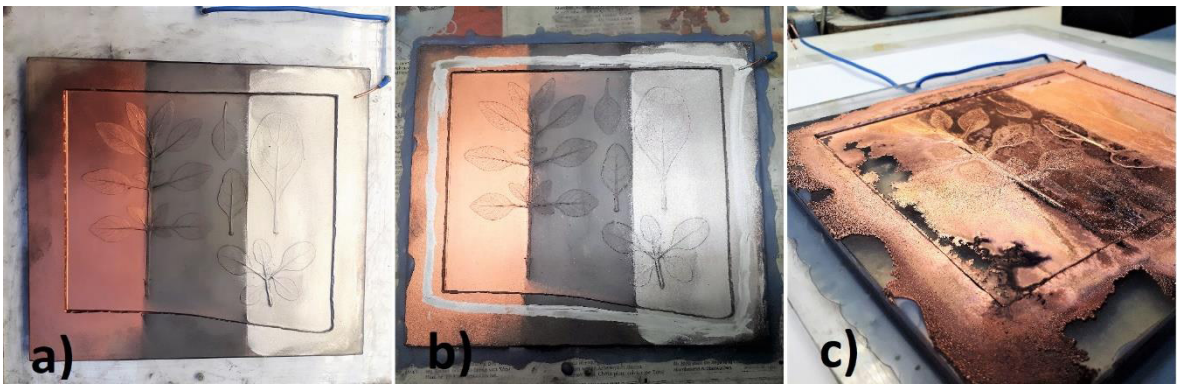

Fig. 9 Siloxane mould. a Left section coated with Gold Bronze Powder 9900 Copper; middle section coated with Graphite Fine Powder extra pure; right section coated with Silver Powder 1000/1000. b Powder coated sample with additional contact silver lacquer electrode and with wax seal to prevent electrolyte penetration. c Electrodeposited copper layers

Polishing of the galvanic copper printing plates has been an established finishing step. A polished object could be used almost twice as long for printing purposes as an unpolished object. Mechanical polishing of the buffed and brushed sample removed various roughnesses on the surface by pressing and rubbing so that the individual asperities were eliminated until the surface appeared mirror smooth. Historically, various tools have been used, namely polishing steel, agate, some types of horn and bloodstone/hematite [13]. Thin galvanic layers were often polished with leather which was coated with a mixture of oil and a hard powder such as pumice stone, tin ash or bloodstone. Later, galvanic objects were polished on the polishing machine with a rotating brush or fabric disc.

It is not clear how Alois Auer polished the obtained printing plates for the production of nature prints. Therefore, in the present work, three surface states were examined. The plate segments, made conductive with silver, graphite and copper powder respectively, were sawn into three segments so that each contained one third of each powder type. One third was polished manually using bloodstone while the second third was polished with a fabric disc on a polishing machine and the last third remained untreated (compare Fig. 12 below). A polishing paste was used with a rotating fabric disc (Baier's Enkel Nfg., Silberglanz-Paste, fat-bound).

Measuring windows of ca. 1 cm² serving as working electrode surfaces were generated on each plate segments by an electrically insulating siloxane adhesive (Saint-Gobain Performance Plastics MG Silicon GmbH, SK 6000 Neutral). Electrochemical measurements were carried out with an Ag/AgCl reference electrode (RE, + 0.222 V vs. SHE [101] and a gold counter electrode in the form of a wire spiral (CE) in a glass tube with a porous frit as electrolyte junction. The cyclic voltammetry and the open circuit transient measurements were performed with an electrochemical workstation (CH Instruments, 760C). A 0.1 M K_2CO_3 (pH = 10.6) solution with deionized water (Milli-Q) served as electrolyte. The pH value was determined by a glass membrane electrode (Metrohm, 780 pH Meter). Before starting the electrochemical measurements, the plate was degreased inside the measuring window by wiping with a cotton swab soaked with acetone.

Optical micrographs were recorded with a digital microscope (Keyence, VHX-5000). Electron micrographs were registered with an environmental scanning electron microscope (FEI, Quanta 250 FEG with a Schottky field emission source).

4.5. Results and Discussion

The metal powders applied on the insulating siloxane moulds constitute the conductive electrodes for the electrodeposition of the copper layers. The morphology, the volume resistivity, and the thickness of the applied metal powders should have an influence on the quality of the electrotypes.

The local current density affects the deposit morphology [102]. It is proportional to the reciprocal of the volume resistivity and the thickness of the applied powder layer at an applied constant potential:

$$j \approx 1/R \approx 1/\rho \times d \quad (1)$$

with the powder layer thickness d (Eq. 1). The volume resistivity of the graphite exhibits the highest value in respect to Cu and Ag (Table 3). Therefore, graphite should exhibit the lowest local current density at constant $d \approx 50\mu m$. The lower the current density the higher the contribution of the base reproduction growth type versus the field-oriented type will be. This leads to a smooth and small-grained deposit for graphite (Fig. 10 and 11, Table 3).

When a base reproduction occurs at moderate inhibition intensity by an additive, the respective powder morphology can have a direct influence on the electrodeposit texture. The base electrode graphite shows the smallest grain size (<15µm) whereas Ag shows greater sizes (>35µm), and Cu a broad distribution of up to 30µm (Fig. 10 and 11, Table 3). Therefore, the observed Cu deposit grain size on graphite resulted in the lowest value (Fig. 10 and 11, Table 3).

Table 3. Conductive powder properties and electrodeposited copper plate grain sizes.

Name	Volume Resistivity, ρ [Ωm], 20°C	Powder Layer Thickness d [µm]	Powder Grain Size [µm]	Cu Deposit Grain Size [µm]
Cu (Gold Bronze Powder 9900)	$1{,}543 \cdot 10^{-8}$ (18)	55.6 ± 8.4	10 - 30	20 -50
Graphite (Graphite Fine Powder extra pure)	$3500 \cdot 10^{-8}$ (18)	47.5 ± 7.0	1 - 15	5 - 20
Ag (Silver Powder 1000/1000)	$1{,}467 \cdot 10^{-8}$ (18)	55.2 ± 17.9	35 – 40	20 - 50

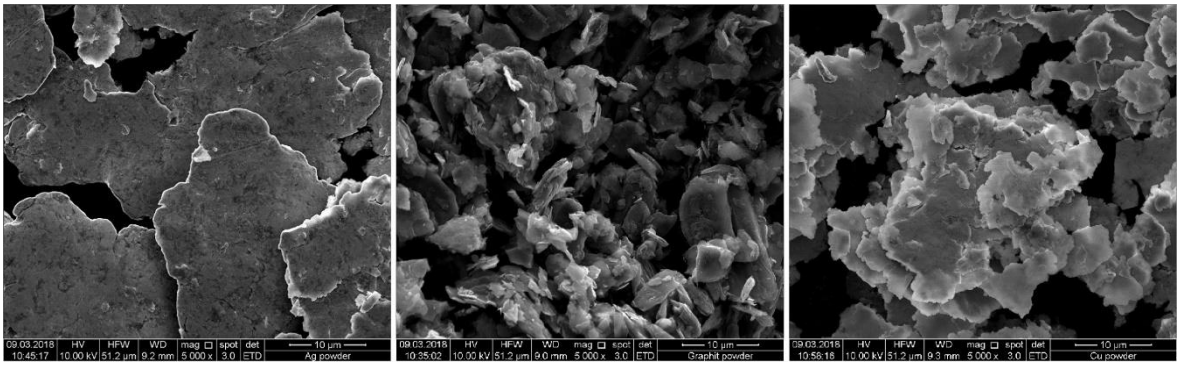

Fig. 10 Scanning electron micrographs of Silver Powder 1000/1000 (left), Graphite Fine Powder extra pure (middle) and Gold Bronze Powder 9900 Copper (right). 10 kV, ×5000

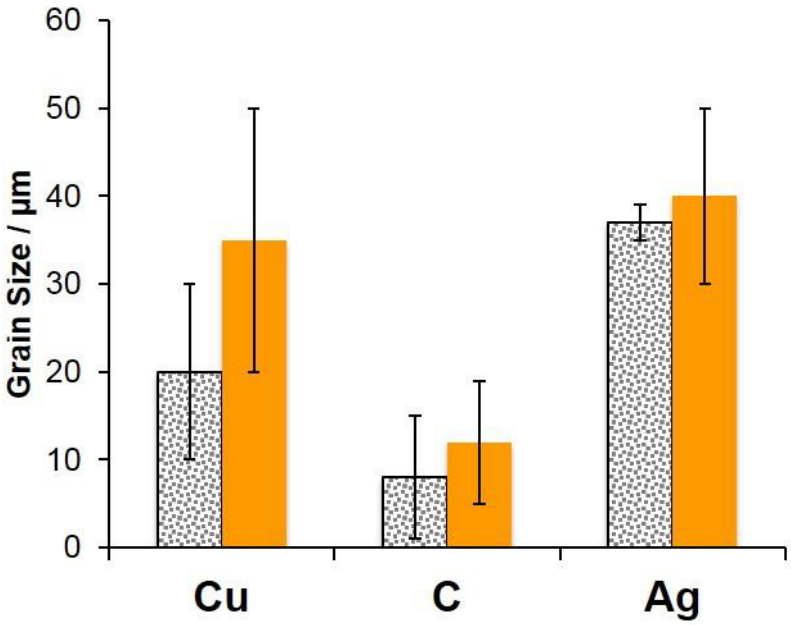

Fig. 11 Conductive powder (dotted) and electrodeposited copper plate (orange) grain sizes

The Cu plate electrodeposited on Cu powder was an incomplete, uneven, and inhomogeneous layer (Fig. 9c and 6). The region near the inhomogeneities were partially delaminated and exhibited darkened and "burned" surfaces. Therefore, electrolyte penetrated also between the Cu deposit and the Cu powder layer on siloxane mould. The Cu edges showed grainy and powdery morphology due to enhanced local current densities. The "burned" surface features can be correlated with high rates of hydrogen discharge [103]. This leads to a pH increase in the interface resulting in the precipitation of hydroxide or basic salts of Cu. These may be occluded by the plated deposit.

Fig. 12 Photograph of the electrodeposited copper printing plate. Vertical column with various conductivity powders on siloxane. Left: Ag. Middle: graphite. Right: Cu. Horizontal rows with various post treatments. Bottom: untreated. Middle: machine polished. Top: hand polished.

The Cu plate electrodeposited on either graphite or Ag powder provided a homogeneous and compact layer (Fig. 12). Powder remnants still adhered visibly in depressions (Fig. 13, Table 4).

The after treatment was performed by hand (stone) polishing using hematite (bloodstone) and machine polishing (rotating fabric disc). The advantages of stone polishing are the higher gloss, the texture of the surface becomes denser, and the metal loss is minimized in contrast to machine polishing. The elevated parts of the surface profile appeared dark in the machine polished regions. This is due to the specular reflection of the illumination light which cannot be collected in the microscopic objective. Fine one-directional scratches were introduced in these flat regions by the rotating fabric disc treatment. Hand polishing yielded much shinier regions without the leaf motifs than machine polishing. Practically no scratches were introduced by the hematite/bloodstone treatment. Hand polishing did not affect the depressed features of the original leaf in contrast to machine polishing. A substantial difference in quality

was observed between the electroformed leaf details of the plate deposited on Ag and graphite: the faithfulness to the original was by far superior on the Cu plate deposited on the graphite base electrode than that deposited on the Ag base electrode. A Cu base electrode resulted in a rough surface. Machine and hand polishing yielded comparable qualities as the Cu plate deposited on the Ag base electrode.

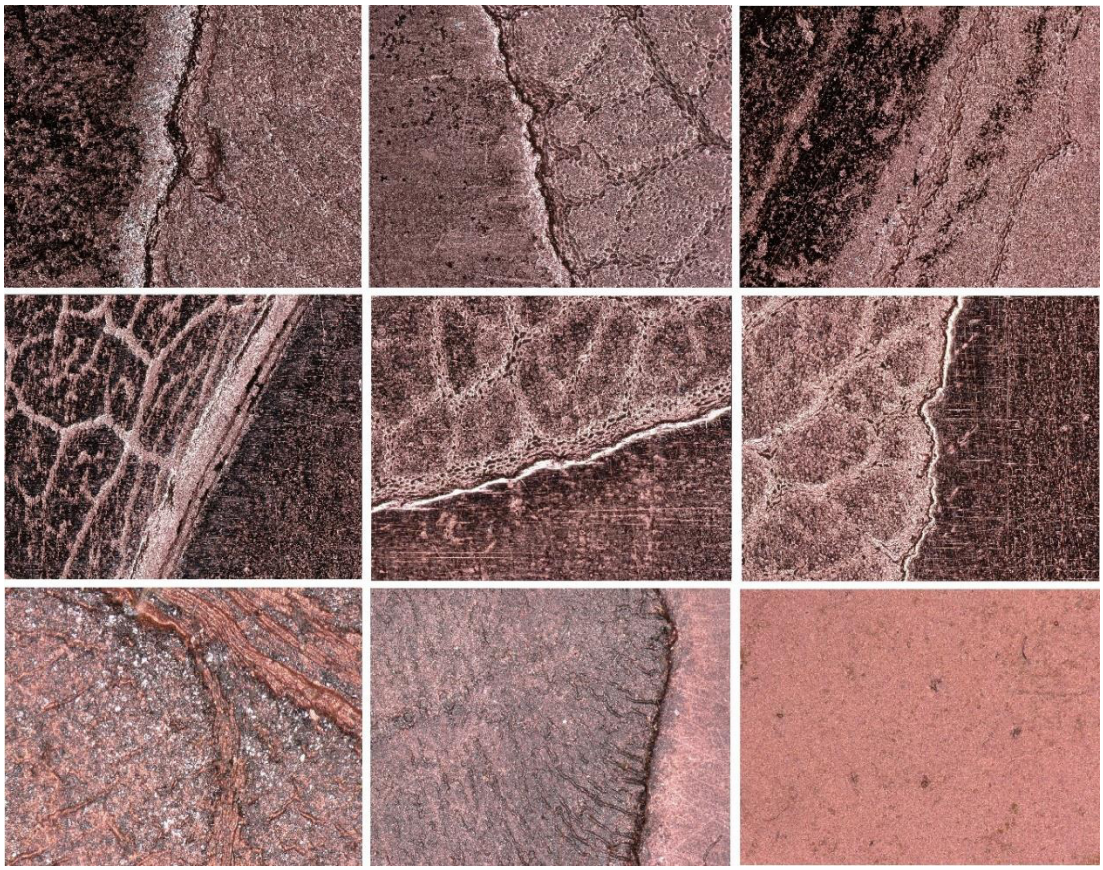

Fig. 13 Optical Micrographs of the moulded side of the electrodeposited copper printing plate. Vertical column with various conductivity powders on silicon. Left: Ag. Middle: graphite. Right: Cu. Horizontal rows with various post treatments. Bottom: untreated. Middle: machine polished. Top: hand polished.

The prints of the three plates separated by their polishing treatment (Fig. 12) showed drastic differences in quality (Fig. 13). The faithfulness to the original leaf motif from the hand polished plate was by far superior to that treated by machine polishing. On the other hand, the background of the print from the machine polished plate was more homogeneous than that from the hand polished. The print from the untreated plate exhibited a good faithfulness to the original leaf motif but showed strong inhomogeneities of the background.

Table 4. Copper deposit characterization

Conductive layer	Untreated	Machine polished	Hand polished
Cu (Gold bronze powder)	Incomplete, uneven, inhomogeneous, burned. Matt appearance.	Incomplete, uneven, inhomogeneous plate. Scratches on elevations. Poor faithfulness to the original.	Incomplete, uneven, inhomogeneous plate. Smoother than machine polished, no scratches. Moderate faithfulness to the original.
Graphite powder	Complete, compact layer. Matt appearance Remnants of graphite powder.	Scratches on elevations. Impaired faithfulness to the original.	Smoother than machine polished, no scratches. Best faithfulness to the original.
Ag (Conductive silver powder)	Complete, compact layer. Matt appearance. Remnants of Ag powder.	Scratches on elevations. Poor faithfulness to the original.	Smoother than machine polished, no scratches. Moderate faithfulness to the original.

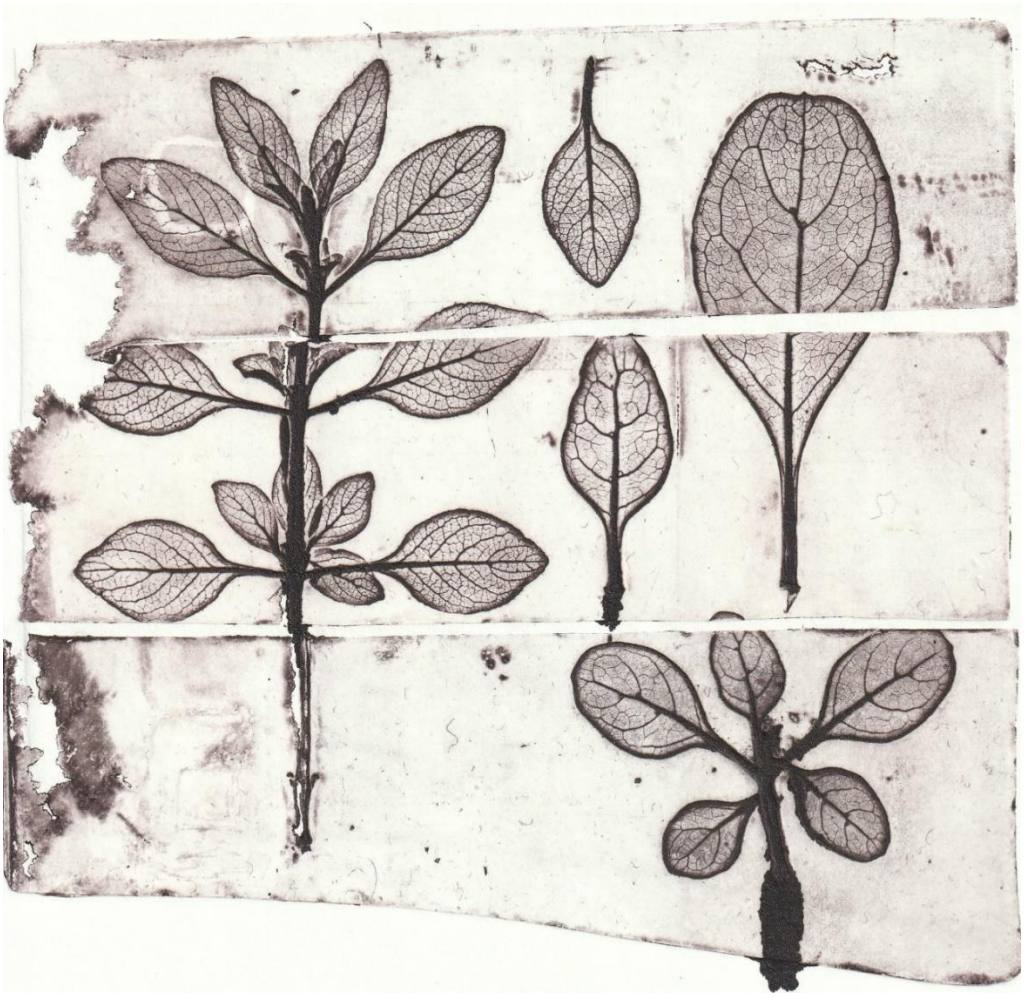

Fig. 14 Photograph of the print on paper derived the plate shown in Fig. 6. Vertical column with various conductivity powders on siloxane. Left: Cu. Middle: graphite. Right: Ag. Horizontal rows with various post treatments. Bottom: untreated. Middle: machine polished. Top: hand polished

Table 5 Reactions of copper in alkaline solution (21)

Reaction	Nernst Equilibrium Potential vs. SHE, U_0	Nernst Equilibrium Potential vs. SHE, U_0 pH = 10.60
$2Cu + H_2O \rightleftharpoons Cu_2O + 2H^+ + 2e^-$	0.47-0.059pH	-0.16
$Cu + H_2O \rightleftharpoons CuO + 2H^+ + 2e^-$	0.57-0.059pH	-0.06
$Cu_2O + H_2O \rightleftharpoons 2CuO + 2H^+ + 2e^-$	0.67-0.059pH	+0.04
$Ag \leftrightarrow Ag^+ \rightleftharpoons e^-$	$0.80+0.059\log[Ag^+]$	~+0.50 ([Ag*] ~ 10^{-5} M
$2Ag + H_2O \rightleftharpoons Ag_2O + 2H^+ + 2e^-$	1.17-0.059pH	+0.54

The remnants of the conductive powder layers on the electroformed Cu printing plate introduce local elements which can accelerate localized corrosion reactions. This can yield enhanced roughness thus impairing the long-term stability and applicability of such artefacts. The faithfulness of prints would be diminished by an increased plate roughness. Also, the graininess in the plate background would be enhanced.

The corrosive behaviour was studied by cyclic voltammetry in a 0.1 M K_2CO_3 solution (pH = 10.6). The Cu oxidation to Cu(I) oxide

$$2Cu + H_2O \rightleftharpoons Cu_2O + 2H^+ + 2e^- \quad (2)$$

and the further oxidation to Cu(II) oxide

$$Cu_2O + H_2O \rightleftharpoons 2CuO + 2H^+ + 2e^- \quad (3)$$

as well as the respective reduction reactions could be detected with remnant Ag, graphite powder, and Cu powder even after machine and hand polishing (Fig. 15). The peak of the Cu_2O formation occurs at a potential positive of the Nernst equilibrium potential of this reaction, U_0 = -0.16 V (Eq. 2, Table 5). The reduction of Cu_2O occurred as a peak between ca. -0.2 and -0.4 V. The oxidation of Cu_2O to CuO supported a broad current wave at U > +0.5 V (Eq. 3, Table 5). The reduction of CuO yielded a peak negative of the respective Nernst equilibrium potential U = +0.04 V. Remnant Ag powder show a strong redox activity and thus introduced a local element. The Ag oxidation on an untreated and a machine polished sample led to peaks at U > 0.5 V. The first may be related to the oxidation to Ag^+ and the second around +0.7 V which is positive of the respective Nernst equilibrium potential U_0 = +0.54 V of the oxidation to silver (I) oxide (Table 5)

$$2Ag + H_2O \rightleftharpoons Ag_2O + 2H^+ + 2e^-. \quad (4)$$

The reduction of Ag_2O yielded negative peaks at U < U_0 = +0.54 V. Machine polishing led to a strongly scratched surface resulting in an increased surface area and higher current densities. The hand polished and untreated surfaces exhibited drastically smaller redox current densities.

These results demonstrate the strong electrochemical activity of Ag powder remnants, even after polishing treatments. Therefore, a local element of this noble metal can cause the dissolution and corrosion of the Cu printing plate. It must be pointed out that hand polishing with hematite/bloodstone resulted in the lowest electrochemical activity in contrast to machine polishing.

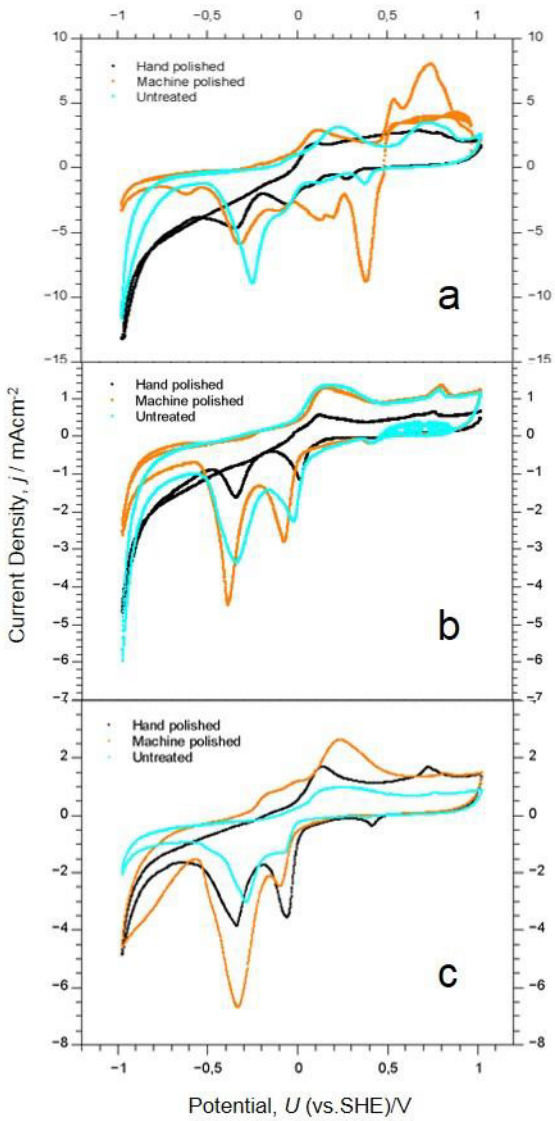

Fig. 15 Cyclic voltammograms of copper plate surface in 0.1 M K2CO3, pH = 10.60. Scan rate = 10 mVs−1. Comparison of a silver, b graphite, c copper powders as conductive layers on the mould. Parameters: polishing methods

4.6. Conclusions

The nature printing technique, originally developed in the 19th century, makes use of plants and other natural subjects to produce images. In the present study, synergistic effects of the cooperation between contemporary art and heritage science in the reconstruction of the historical technique of nature printing are presented. New plates for nature printing were produced using the historic process in order to gain a better understanding of the production technique. The aim was to make individual production steps comprehensible and to find practicable solutions for difficulties encountered in production. One of the main challenges was the production of electrodeposited copper printing plates usually preceded by the coating of the motif with an electrically conductive material. Three different conductive layers, copper, graphite and silver powders, were investigated in respect to their efficacy by morphological investigations using electron microscopy, optical microscopy, and cyclic voltammetry. The suitability of the electrochemically deposited printing plates could be related mainly to the various grain sizes and the electrical conductivities of the investigated conductive powders, as well as the polishing treatments. It could be confirmed that graphite is the best electrochemical conductor in the manufacture of printing plates with high faithfulness to the original motif.

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II. Highly Photosensitive Daguerreotypes and their Reproduction: Physico-chemical Elucidation of Innovative Processes Developed Around 1840 in Vienna

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Contributions:
After my extensive historical research, the uniqueness of this photo printing plate was recognized. Together with W. Kautek, I further developed the idea, conceived the experiments and compared them with the literature and established the context to previous findings about early photography. I carried out the light microscopic examinations on the original plate. SEM/EDX were carried out together with at the University of Applied Arts Vienna. Both authors gave critical feedback, helped to shape the research aspects and contributed to the research, analysis and the manuscript.

Keywords: daguerreotypes, heritage science, photochemistry, photography, nanoparticles.

4.7. Abstract

A physico-chemical elucidation of the world-wide first photographic technology allowing manifold reproduction is presented. An etched daguerreotype manufactured around 1840 in Vienna, preserved by the Technisches Museum Wien, served as a case-example. Surface analysis showed that the photographic process involved the formation of colloidal Ag nano-particles (AgNPs) with sizes of 30-120nm with shell layers consisting of Ag_2O, Ag_2S, and some AgCl. The breakthrough photographic technique provided a hitherto unachieved high sensitivity due to various halogenide mixtures without Hg. The image development consisted in the reduction of the Ag halides by H_2SO_3 created by the hydrolysis of S_2Cl_2 leading to AgNPs adjacent to the latent image Ag nuclei. The fixation of the image was performed either by KCN or by $Na_2S_2O_3$. The investigated plate exhibits etched areas with Ag_2O conversion layers and no Cl or S. The first reproduction method for daguerreotypes was invented by Joseph Berres in Vienna. It consisted in etching to enable printing. He applied a gum arabic solution on the fixed image surface. The gum Arabic preferentially wetted the exposed AgNP regions so that unexposed areas could be etched by HNO_3.

4.8. Introduction

The French artist Louis Jacques Mandé Daguerre is considered the inventor of early photography [38–40,104–106]. His invention, publicly reported 1839 in Paris, marked the decisive step in the development of reproduction technology. During the preparation of the daguerreotype, a silver-plated surface was sensitized by silver iodine vapour and exposed to light in a camera. Then the plate was fumigated with mercury vapour and permanently fixed with a hot sodium thiosulfate solution [38,107–109]. At the beginning of the daguerreotype, long exposure times were a hindrance for the creation of the portraits and moving scenes like street views. On the one hand, this was due to the low light's optics available at the time, and on the other hand, to the relatively weak photosensitivity of the iodized silver surface. In order to reduce the exposure time and improve the photographic quality, further fundamental chemical and physical inventions had to be made [110]. Shortly afterwards, at the beginning of 1840is, remarkable inventions in the field of early photography have also been made in Vienna [41,111–115]. Josef Maximilian Petzval, a professor for mathematics, designed the very first photographic portrait objective lens (Fig. 16) [41,112,113,116,117]. This was the first mathematically calculated precision objective lens in the history of photography. Petzval's

revolutionary dual lens exhibited a much higher luminous intensity and was more powerful than Daguerre's camera lens allowing exposure times of less than a minute. The lens was manufactured by the Viennese optician Peter Wilhelm Friedrich von Voigtländer. He developed a new camera equipped with Petzval's objective which was sold successfully worldwide.

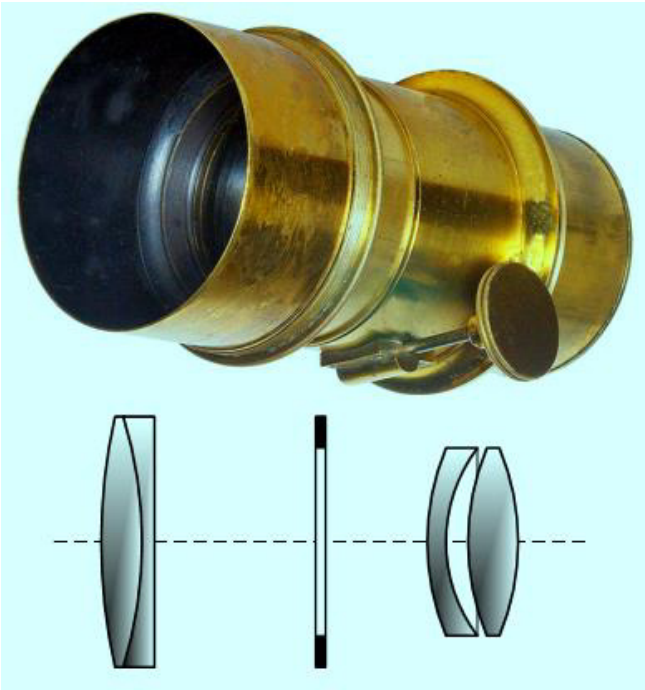

Fig. 16 Petzval lens (objective). The first photographic portrait objective lens in the history of photography [18]. ©Tamasflex.

Moreover, the Viennese photographic pioneers Franz Kratochwila and the medical doctors the brothers Johann and Josef Natterer developed new sensitization procedures in 1840/41 deviant from techniques applied in other countries [111–113,117]. In order to improve the poor light sensitivity of the iodized silver surface used by Daguerre, they developed sensitization procedures employing mixtures of bromine, chlorine and iodine applied in various sequences and compositions (Table 6). In this way snapshots could be taken for the first time [112]. The first two worldwide known photographs of street scenes and people crowds originate from them [40,41,113]. A representative fuming box and laboratory utensils for daguerreotype are depicted in Fig. 17a and Fig. 17b, respectively. In addition, the Natterer brothers developed another procedure omitting mercury used in common daguerreotype [112].

Fig 17 left. Fuming box for daguerreotype, Inv.Nr.: 2112, Technisches Museum Wien, Austria. **right.** Wooden box with laboratory utensils for daguerreotype, 1839 Giroux Paris, Inv.Nr.: 2110, © Technisches Museum Wien, Austria.

Table 6. Daguerreotype processing steps reported in literature

Processing steps	Chemical reaction	Physical-chemical changes at the surface
Coating the copper plate with Ag		
Polishing		
*Sensitization with I_2 (Daguerre) [38,40,110] **Multiple sensitization [38,111–114]: $I_2 \rightarrow Br_2 \rightarrow I_2$ (J.F. Goddard 1840) $I_2 = Br_2$; $Cl_2 = Br_2$; $I_2 = Cl_2$; $I_2 \rightarrow Cl_2$ (F. Kratochwila, J. & J. Natterer, E. Waidele 1840/41) $I_2 \rightarrow Br_2 \rightarrow Cl_2$ (F. Kratochwila, J. & J. Natterer 1840/41)	$2Ag_{(s)} + Cl_{2(g)} \rightarrow 2AgCl$ $2Ag_{(s)} + I_{2(g)} \rightarrow 2AgI$ $2Ag_{(s)} + Br_{2(g)} \rightarrow 2AgBr$	Chemical acceleration of the Ag surface. The surface is covered with Ag halogenide crystals. Halogenide mixture provides higher light sensitivity and shortens exposure time. AgCl – white appearance AgI – yellow appearance AgBr – cream yellow appearance
Exposure of silver halides (AgX)	$10AgX + hv \rightarrow 2Ag_{(s)(5)} + 5\ X_{2(g)}$	Decomposition of silver halides by light and formation of silver clusters (latent image formation).
Developement by Hg vapor ~ 60 bis 120° C (L. Daguerre 1839) Development without Hg (H. Becquerel 1840) [38]	$11Ag_5 + 45Hg_{(g)} \rightarrow 5Ag_{11}Hg_9$ $3Ag_5 + 20Hg_{(g)} \rightarrow 5Ag_3Hg_4$	Silver react with hot mercury droplets and form stable amalgam. Development without Hg (H. Becquerel 1840) [38] Latent image developed by a yellow and/or red light treatment.
Fixation by sodium thiosulfate (J. Herschel 1839) [38,40,104,113,114]	$2\ Na_2S_2O_3 + AgX \rightarrow Na_3[Ag_8S_2O_3)_2] + NaX$	Dissolution of unexposed residual silver halides.
Post cleaning with water		Removal of the residual fixing solution.
Gilding or toning with a AuCl solution [38,40,104,113,114]	$[Au(S_2O_3)_2]^{3-} + Ag \rightarrow Au + [Ag(S_2O_3)_2]^{3-}$	Increasing contrast and brilliance of the image.
Post cleaning with water		Removal of the residual gold chloride solution.

The Austrian anatomy professor Joseph von Berres was interested in the generation of micrographs as a tool for microscopic research [113,118]. He recognized the potential of the newly discovered daguerreotype technique [119–122]. Since a daguerreotype is a unique object, Berres saw the need for the development of a reproduction technique. Already in 1840 [40], he succeeded in producing printing plates for the first reproduction of photographs

by etching daguerreotype plates. This etching technique is still widely unexplored, because no original etched daguerreotype plates have been discovered by now. The knowledge of the physico-chemical processes associated with the above mentioned new photographic techniques is rudimentary up to date. The present study of the fundamentals of the above-mentioned novel procedures could be based on investigations of an etched daguerreotype plate probably photographed by the brothers Natterer and etched by Berres. It was recently discovered in the collection of the Technische Museum Wien [75]. This carrier plate is a silver-plated copper sheet typical for daguerreotypes and shows Joseph II's equestrian monument on Josefsplatz in Vienna (Fig. 18 left). Joseph II, the eldest son of the Austrian ruler Maria Theresa, was a Holy Roman Emperor and took over the Habsburg lands from his mother in 1780.

Fig. 18 Joseph II's equestrian monument on Josefsplatz. Vienna. Etched Daguerreotype, Inv.Nr.: 83939/18, © Technisches Museum Wien, Austria. Plate size: 127 x 144 x 1 mm. **Left**: photograph. **Right:** inverted and horizontally mirrored photograph.

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4.9. Results and Discussion

4.9.1. Surface Characterization

Surface characterization investigations were conducted in order to elucidate the manufacturing processes of daguerreotypes in Vienna of the early 1840s. The plate of the Joseph II's equestrian monument on Josefsplatz in Vienna retained its metallic brilliance (Fig. 18 left). The excellent depth of field and image quality despite the existing etched surface regions and various signs of aging can be best recognized by an inverted and horizontally mirrored photograph of the plate which represents the actual aspect on Josefsplatz. There, the camera was set up south of the monument at a window of Augustinertrakt, a side wing of the Hofburg, the former principal imperial palace (Fig. 18 right).

Optical micrographs and surface profilometry (Fig. 19) show that the daguerreotype plate represents an etched daguerreotype plate most probably designated for printing reproduction. Various profile levels - and even a flaw due to possibly an etchant splash - suggest this conclusion. The etched depressions are comparatively flat with a maximum depth of up to 6 µm. A scanning secondary electron micrograph of the plate is shown in Fig. 20. In an EDX analysis, the primary electron beam interacts with the sample by repeated random scattering leading to a teardrop-shaped volume extending from less than 100 nm to approximately 5 µm into the near-surface region. The depth of this interaction volume depends on the electron's landing energy, the atomic number of the specimen and the specimen's density. The depth of the x-ray (EDX) activation, h can be appreciated by the following equation [123]

$$h = 0.0276\ m_a\ V^{1.67} / z^{0.89}\ \rho\ [\mu m] \qquad (5)$$

where m_a = atomic weight (g/mole), ρ = density (g/cm^3), z = atomic number, and V = electron acceleration voltage (kV). With a V of 20 kV and the respective values of Ag this relationship results in an EDX activation depth of ca. 1.4 µm. The silver coating on the copper substrate plate showed an average thickness of 7.3 ± 1.1 µm determined by an array of 36 x-ray fluorescence measurements spots. That shows that solely the Ag coating with an average thickness of 7.3 ± 1.1 µm has been analysed by EDX. A case with finite Cu signals would suggest pores and/or inhomogeneities (e.g. due to etching) in the Ag layer.

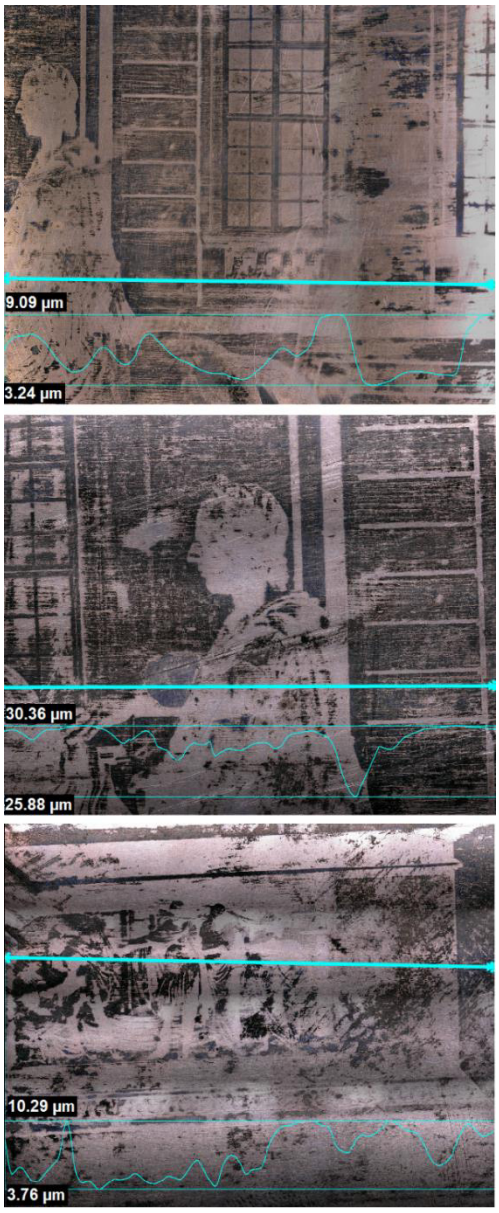

Fig. 19 Optical micrographs with profilometry of the etched daguerreotype (Fig. 18). Three profile lines. Horizontal image edge: 513 mm (upper), 387 mm (middle), 272 mm (bottom).

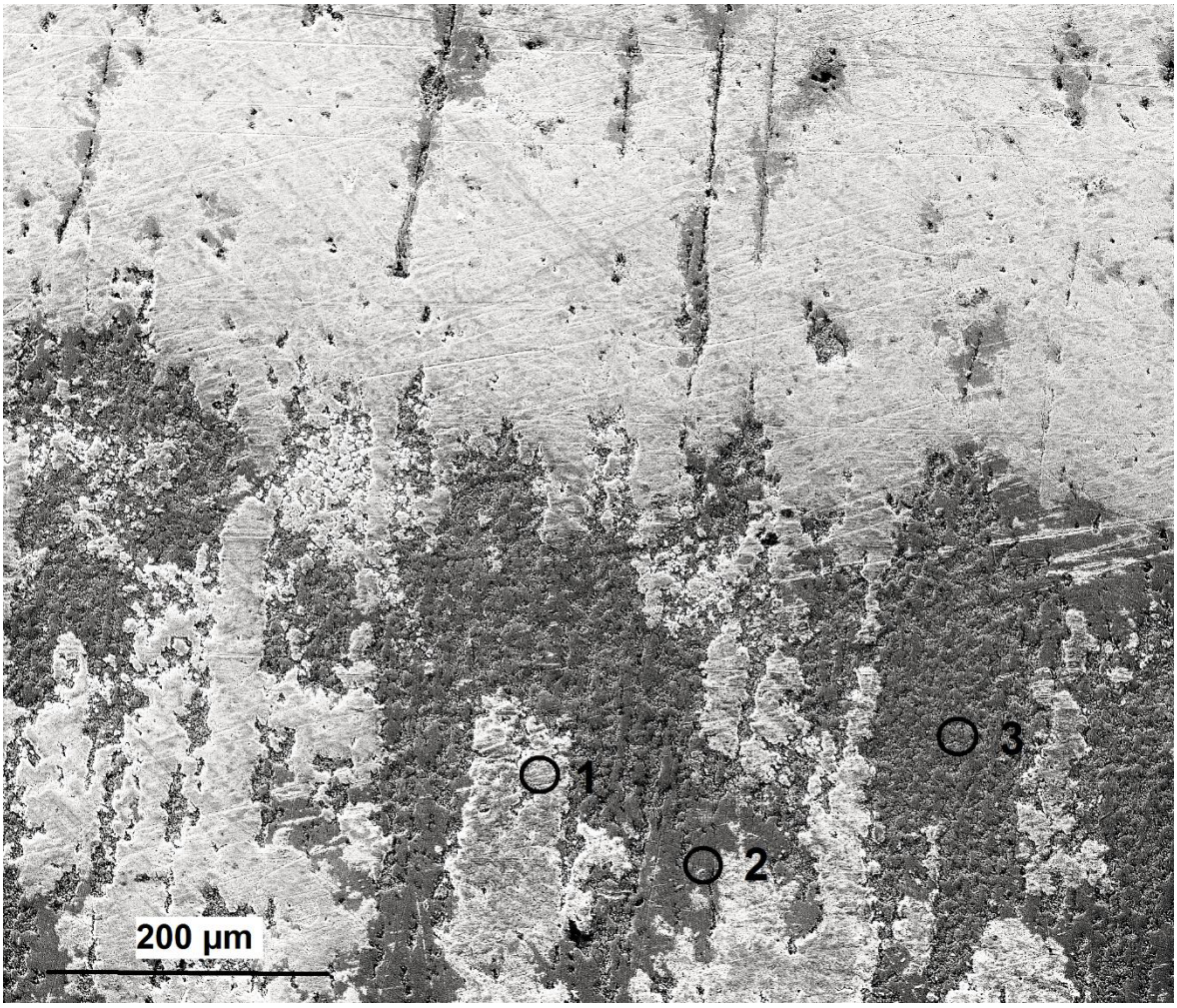

Fig. 20 Scanning secondary electron micrograph of the etched daguerreotype (Fig. 18). Detail of the hoof front of the horse's right hindquarter. Three SEM/EDX measurement point are indicated.

Three SEM/EDX measurement points were chosen in the area of the hoof front of the horse's right hindquarter (Fig. 20). Three distinct morphological regions could be identified. Region 1 shows the highest secondary electron signal in contrast to region 2 and 3. This may suggest that the work function of this surface is lower than that of region 3, or/and that its lower conductivity leads to electron charging. A work function difference can be due to a different chemical composition of area 1 at variance to 2 and 3. The morphology of region 3 is typical for an etched surface which corresponds to low light exposure in contrast to the high exposure area 1 which does not exhibit etching features.

Table 7. EDX results (at%) of the regions 1-3 indicated in Fig. 20.

	Region 1	**Region 2**	**Region 3**
S	14.39	0	0
Cl	1.10	0	0
Cu	1.35	1.27	3.63
O	4.37	8.05	20.86
Ag	38.72	52.74	37.56
C	38.97	37.26	37.37
Si	0.57	0.68	0.57
P	0.53	0	0

Region 1 represents a well light-exposed area where the photographic process based on silver halogenides led to the photon-catalysed reduction to colloidal silver nanoparticles (AgNPs). This photoproduct can be clearly seen in Fig. 21 left. The observed particle size distribution is between 30 nm and 120 nm, which is less than in characteristic daguerreotype highlight image microstructures between 100 nm and 2.5 µm [38,105]. Particularly the top AgNPs appear light and blurred indicating electronic charging possibly due to core-shell NP morphologies with insulating shell compositions. Such chemical conversions of the Ag core can be recognized by the EDX analysis resulting in a significant sulphur and a moderate chlorine signal besides oxygen (Fig. 21 right, Table 7). This finding suggests that the colloidal particles exhibited a conversion shell layer consisting of Ag_2O, Ag_2S, and some AgCl with low conductivity.

These AgNPs and their conversion shells are practically absent in the midtone (Region 2) and dark tone (Region 3) areas (Fig. 20). The midtone region shows only some scratches from the original polishing treatment and some etching bits with diameters of < 100 nm (Fig. 22 left). The dark tone areas, in contrast, are dominated by larger etching bits with diameters of 200 – 400 nm (Fig. 23 left). Original polishing scratches are still observable despite extensive etching, however widened. The EDX analysis showed that any conversion layers involving Cl or S are absent (Fig. 22 right, 8 right, Table 7). The increased oxygen signal of the most extensively etched surface (Region 3, Fig. 23 right, Table 7) indicates a more abundant Ag_2O layer. The etching process exposed some copper substrate which is indicated by a somewhat higher Cu signal.

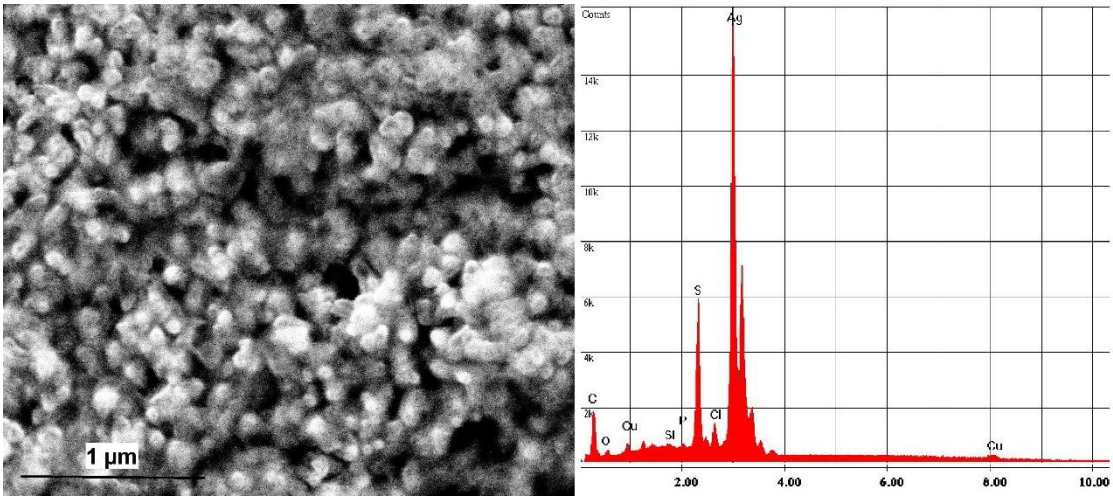

Fig. 21 Scanning secondary electron micrograph (left) and EDX spectrum (right) of the etched daguerreotype (Fig. 18). Measurement point 1 in the white highlight.

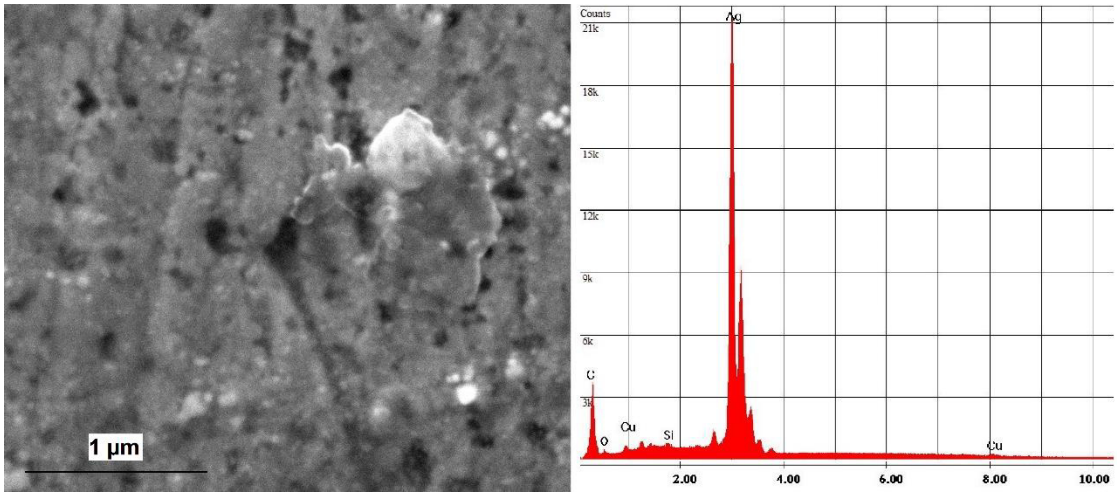

Fig. 22 Scanning secondary electron micrograph (left) and EDX spectrum (right) of the etched daguerreotype (Fig. 18). Measurement point 2 in the midtone area.

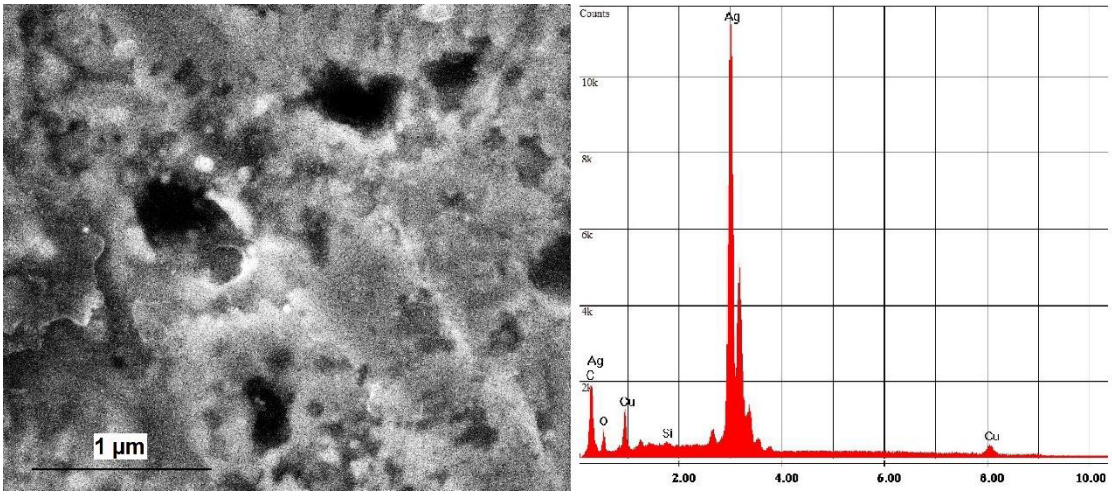

Fig. 23 Scanning secondary electron micrograph (left) and EDX spectrum (right) of the etched daguerreotype (Fig. 18). Measurement point 3 in the shadow area.

4.9.2. Photographic Procedure reconstruction

Silver Coating of the Copper Plate

Solid silver plates were rarely used [112]. In the beginning 1840ies galvanic silver plating was employed [38] and were available at relatively high costs in Vienna. Therefore, Kratochvila, J. and J. Natterer chose also electroless plating [13,74]. AgCl was dissolved in a NaCl solution [60]. Solid AgCl can form a chloroanion in the presence of highly concentrated Cl^- [81,124]

$$AgCl + Cl^- \rightarrow [AgCl_2]^- \quad (6)$$

The electroless reaction was the cementation of Ag from the dichloro silver anion on the copper plate. This is thermodynamically driven by the oxidative power of the silver electrode [101]:

$$Ag \rightleftharpoons Ag^+ + e^- (U_0 = +0.80\ V) \quad (7)$$

with a standard potential U_0 which is much more positive than that of the Cu dissolution reactions

$$Cu \rightleftharpoons Cu_2^+ + 2\ e^- \qquad (U_0 = +0.34\ V) \quad (8)$$

$$Cu \rightleftharpoons Cu^+ + e^- \qquad (U_0 = +0.52\ V) \quad (9)$$

The overall electroless silver plating reaction (a cementation reaction) is therefore

$$[AgCl_2]^- + Cu \rightarrow Cu^+ + 2\ Cl^- + Ag \quad (10)$$

or

$$2\ [AgCl_2]^- + Cu \rightarrow Cu_2^+ + 4\ Cl^- + 2\ Ag \quad (11)$$

Sensitization

The first sensitization process based on the Daguerre's experience was the fumigation of the polished silver surface with iodine vapour [38,40,104,113] in a special fuming box (Fig. 17 left). There, photosensitive AgI was generated by the oxidation of the Ag substrate [105] (Table 6). However, iodine does not exhibit a sufficiently positive electrochemical potential for this reaction. An indirect route via the oxidant iodate can be suggested. It is well established that aqueous iodine chemistry is mainly governed by three reactions [110,125], namely the disproportionation of iodine to hypoiodous acid HIO, or hypoiodide IO^- anions (oxidation state +I), and to iodide,

$$I_2 + H_2O \rightarrow I^- + IO^- + 2\ H^+. \quad (12)$$

Hypoiodide is not stable and disproportionates to iodate (oxidation state +V) and iodide,

$$3\ IO^- \rightarrow 2\ I^- + IO_3^- \qquad (13)$$

The overall reaction is

$$3\ I_2 + 3\ H_2O \rightarrow 2\ I^- + IO_3^- + 6\ H^+ \qquad (14)$$

The oxidative power of the IO_3^- ion is sufficient at all applied pHs (mostly near neutrality) [126,127] to oxidize the Ag surface so that AgI can be formed as a photosensitive film:

$$6\ Ag + IO_3^- + 6\ H^+ \rightarrow 6\ AgI + 3\ H_2O \qquad (15)$$

AgI exhibited a very low sensitivity[38,40].

A multiple sensitization by fumigation with bromine in addition to iodine was introduced practically in parallel by laboratories in England and Austria yielding an improved sensitivity [40,104,111,113]. Bromine, in contrast to iodine shows a sufficiently positive standard potential [101]:

$$Br_2 + 2e^- \rightleftharpoons 2\ Br^- \qquad (U_0 = +1.0873\ V) \qquad (16)$$

so that Ag (U_0 = +0.80 V) can be oxidized directly to the photosensitive phase AgBr.

The Viennese pioneers, F. Kratochwila, the brothers Natterer, and E. Waidele, extended the multiple sensitization procedures of photographic plates with chlorine gas[111–113,115]. They employed Cl_2 and Br_2 or I_2 concurrently, or in a series, first I_2 followed by Cl_2, or first I_2 followed by Br_2 and finally Cl_2.

The iodized surface was exposed to Cl_2 gas produced by a chlorinated lime ("Chlorkalk"), a mixture of calcium hypochlorite, $Ca(OCl)_2$, $CaCl_2$ and a $Ca(OH)_2$ solution [111]. The reactant of this mixture is CaCl (OCl). It can react with an acid such as carbonic acid from the atmospheric CO_2 producing Cl_2:

$$CaCl\ (OCl) + CO_2 \rightarrow CaCO_3 + Cl_2. \qquad (17)$$

Cl_2 easily can oxidize the Ag surface due to its very positive potential

$$Cl_2 + 2e^- \rightleftharpoons 2\ Cl^- \qquad (U_0 = +1.36\ V) \qquad (18)$$

resulting in an AgCl film.

Exposure

The Viennese authors thus employed a silver halogenide (AgX) mixture as photosensitive phase [111]. The absorption of a photon results in the formation of a latent image based on Ag4 clusters [128]. A photoreaction can be assumed as follows:

$$8\ AgX + 4\ h\nu \rightarrow 2\ Ag_4 + 4\ X_2 \qquad (19)$$

The exposure time in a Voigtländer's Camera Obscura was only within 5 s to 6 s in cloudy weather, within 2 s on a bright day, and in direct sunlight in an “unmeasurable” time. This novel technology allowed the unblurred high quality imaging of moving motifs such as portraits and street scenes for the first time.

Development

The common development procedure for daguerreotypes was the formation of Ag amalgam particles next to the latent image Ag clusters [38,129]. The heated Ag plate was treated by Hg vapour.

Edmont Becquerel reported a development procedure based on AgI without the use of mercury in 1840. This method is related to the famous “Becquerel effect” [130] where AgI was exposed resulting in a latent image. This was further developed by a yellow and/or red-light treatment. However, this ground-breaking invention did not yet assert itself against the method of Daguerre employing mercury [38,40,113].

In the following year, in 1841, also the Viennese Natterer brothers developed a method without mercury [112]. This novel procedure represented a breakthrough photographic technique due to the high sensitivity of the employed halogenide mixture. In the case of the least sensitive layer of AgI, a development procedure was reported [115]. This development process can be reconstructed as follows (comp.[131,132]):

$$2\ S_2Cl_2 + 2\ H_2O \rightarrow SO_2 + 4\ HCl + 3/8\ S_8. \qquad (20)$$

The resulting SO_2 vapour reacts at the surface in humid atmosphere to sulphurous acid:

$$SO_2 + H_2O \rightarrow H_2SO_3. \qquad (21)$$

It is remarkable that the deposition of the developer substance, sulphurous acid, was applied before the exposure. The sulphurous acid obviously acted as a reductant for the Ag halide (AgX) leading to AgNPs around the latent image Ag nuclei:

$$2\ AgX + H_2SO_3 + H_2O \rightarrow 2\ Ag + 2\ HX + H_2SO_4 \qquad (22)$$

The development process already took place in the camera [28].

The authors even used sulphur bromide instead of sulphur chloride,

$$2\ S_2Br_2 + 2\ H_2O \rightarrow SO_2 + 4\ HBr + 3/8\ S_8, \qquad (123)$$

and claimed a superb sensitivity [117].

Fixation

Josef Natterer performed the fixation either by potassium cyanide, KCN, or by sodium thiosulphate[117], $Na_2S_2O_3$. The fixation consisted in the dissolution of remnant halides:

$$2\ Na_2S_2O_3 + AgX \rightarrow Na_3[Ag(S_2O_3)_2] + NaX \quad (24)$$

$$4\ KCN + 2\ AgX \rightarrow 2\ K[Ag(CN)_2] + 2\ KX \quad (25)$$

Etching

The Viennese Joseph Berres succeeded in developing an etching technique in 1840 enabling first reproductions of the newly invented photographs [119–121,133]. He observed that the exposed Hg/Ag areas showed a high resistance towards etching with nitric acid. The unexposed areas covered by unreacted AgX could be attacked by the acid. His treatment of the exposed plates consisted of two operations, (1) the permanent fixation of the image and (2) the etching. The special image fixation procedure is passed down as follows [120].

Berres's fixation deviated from Natterer's procedure in that it prepared the follow-up etching step. The treatment of the plates in HNO_3 led to some dissolution of Cu at the reverse side and Ag on the exposed front side:

$$3\ Cu + 2\ NO_3^- + 8\ H^+ \rightarrow 3\ Cu_2^+ + 4\ H_2O + 2\ NO \quad (26)$$

$$3\ Ag + NO_3^- + 6\ H^+ \rightarrow 3\ Ag^+ + 3\ H_2O + NO \quad (27)$$

Due to its corrosive and oxidative effect, nitric acid is often used in printing technology for etching and is the oldest known mordant.

After fixing the image, Berres continues with the etching process [120].

In this second operation step (the "etching" step), a gum arabic solution was applied on the fixed image surface. Gum arabic, a mixture of glycoproteins and polysaccharides mainly consisting of arabinose and galactose, showed different wetting on the exposed AgNP regions and the unexposed bulk Ag regions. Obviously, the wetting was drastically reduced on the unexposed polycrystalline Ag region so that the follow-up etching step preferentially attacked the substrate. The formed depressions could accept the printing ink in the follow-up reproduction step. On the other hand, the exposed AgNP regions were much more wetted and thus protected by a stable gum arabic film.

In his report on the new developements in daguerreotype [117], Berres pointed to an important detail in the preparation of daguerreotype plates destined for later etching. Although it has been claimed that any carefully applied cleaning method or any cleaning agent could

achieve a pure plate and a satisfactory image, he points out that the challenge of the daguerreotype process lies in the cleaning of the plates. Two techniques by Kratochwila and the physicist Anton Martin (1812-1882) were rated by him as the most reliable ones. Kratochwila simplified and shortened the time-consuming cleaning process by cleaning the polished plate with a distilled turpentine oil and cotton, followed by polishing with a bale of deerskin. Martin cleaned the plates with ethyl alcohol, distilled water, and powdered sheep bones on a soft deerskin. According to Berres, Martin's images exhibit an unsurpassed clarity and sharpness, and are recommended for the production of heliographies destined for printing. The turpentine-treated plates often still had a mist that made the image less pure and, due to a fine resin coating, prevented deeper penetration of the etching process [117].

Berres improved his etching procedure [117]. Obviously, Berres experimented also with amalgamated images [117]. The etch process was repeated until a sufficient depth was reached and was finished by rinsing in distilled water. He was able to achieve hundreds of prints[117]. Berres further reproduced original etched photographs by a process in which an auxiliary intermediate film of Au was electroplated from $AuCl_3$, and numerous Cu replica could be generated by electrotyping. Thus, innumerable photographic reproductions were possible for the first time.

4.10. Deterioration

Deterioration processes generally observed with common daguerreotypes which contain Hg are absent in the present case. The plate does not contain Hg due to a different fixation process. Moreover, due to the absence of cover glasses – as were used with daguerreotypes – no influence of glass corrosion exists. Since the plate was kept completely open and without any protection during the long period of about 180 years, other corrosion processes could be observed in the present study.

The front side of the plate appears yellow-brownish in the middle and blue-greyish at the blurry edges (Fig. 18 left). It is not known whether the plate was smudged during the manufacture and etching process, or at a later stage, due to inadequate storage and handling. Particularly the left edge of the plate and the pavement area were strongly blurred. In addition, scratches, finger smudges and other blurred areas are visible as fine, dark and grey lines and spots. Due to the numerous grey scales and blurred areas, it was very difficult to distinguish

between the physical damages and the chemical alterations of the surface. This suggests that complex deterioration mechanisms took place [38,107].

Unevenness's are visible on the back of the plate (Fig. 24). In the recesses there are residues of a dark coating (probably asphalt).

Fig 24 Reverse side of the etched daguerreotype (Fig. 18).

Along the right front side (Fig. 18 left), approx. 15 mm from the edge, a dark stripe can be observed, which probably comes from the mechanical fixture.

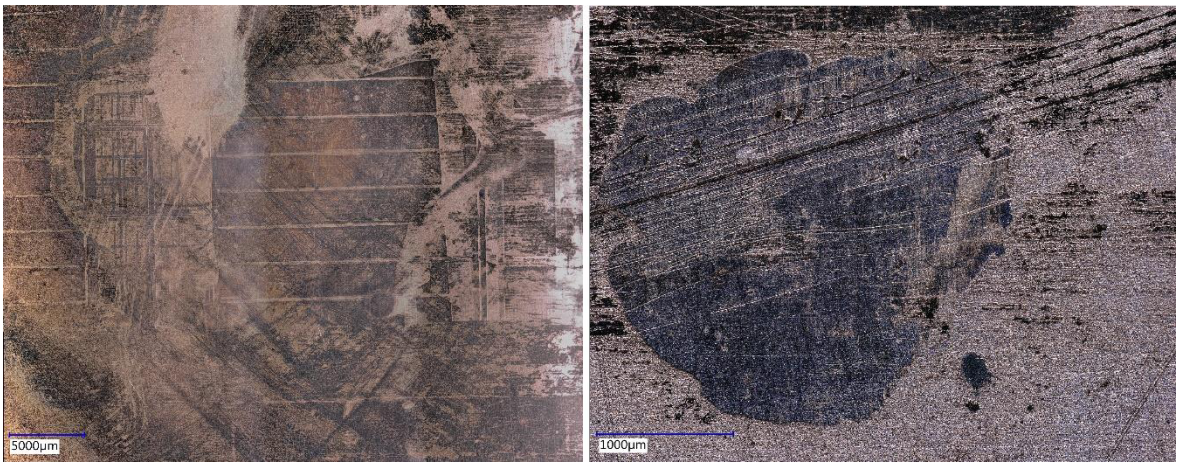

Fig 25 Optical micrographs of a spot-like deteriorated area of the etched daguerreotype (Fig. 18).

Examples of mechanical damages, such as scratches and wiped areas, are presented in Fig.10. Such damages are most probably old and may date back to the time of image production. Several deteriorations exist which look like remnants of splashes. A representative example on the hoof front of the horse's left hindquarter (comp. Fig. 3) is depicted in Fig. 25. A SEM image of another splatter reveals the etched morphology within that area (Fig. 26). This may allow the conclusion that the splashes may have been created during or shortly after the production process unintendedly by an etching liquid such as HNO_3.

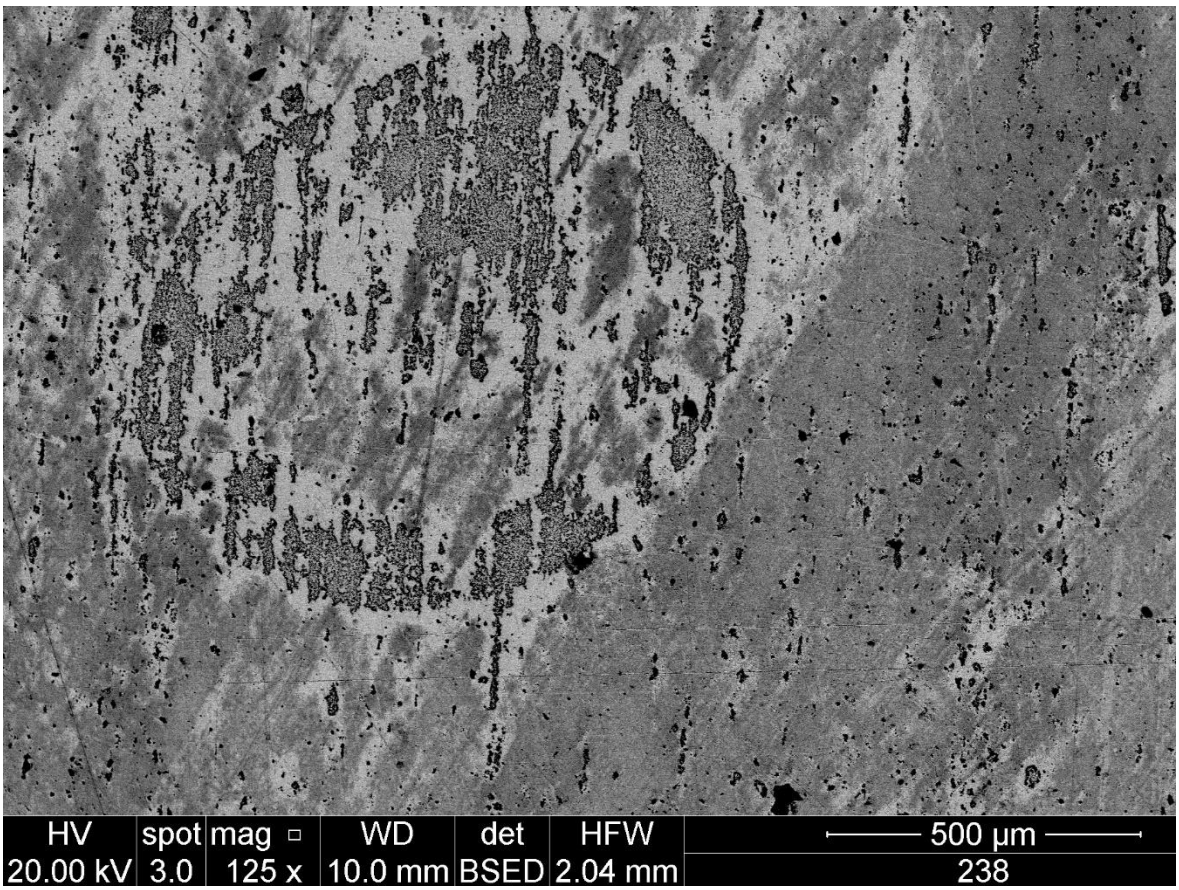

Fig 26 Scanning secondary electron micrograph of a spot-like deteriorated area of the etched daguerreotype (Fig. 18).

4.11. Summary

The physico-chemical fundamentals of the world-wide first photographic technology which allowed manifold reproduction has been evaluated (Table 8). This was performed by detailed investigations of a silver-plated copper plate daguerreotype, recently discovered in the collection of the Technisches Museum Wien. It depicts Joseph II's equestrian monument on

Josefsplatz in Vienna created most probably by the Viennese photographic pioneers, the brothers Natterer and Joseph Berres. Thus, the chemical processes involved could be identified.

The first sensitization process based on the Daguerre's experience was iodization resulting in the photosensitive film of AgI. A drastically improved sensitivity was achieved by multiple sensitization with bromine and chlorine. The remarkable invention by the Viennese pioneers, F. Kratochwila, the brothers Natterer, and E. Waidele, consisted in the multiple sensitization of the photographic plates with chlorine gas. This then oxidized Ag to AgCl.

Table 8. Photographic procedure reconstruction.

Process	Reaction
Ag coating of the Cu plate	$2\ [AgCl_2]^- + Cu \rightarrow Cu_2^+ + 4\ Cl^- + 2\ Ag$
Sensitization	$2\ Ag + X_2 \rightarrow 2\ AgX$
Exposure	$8\ AgX + 4\ h\nu \rightarrow 2\ Ag_4 + 4\ X_2$
Development	$2\ AgX + H_2SO_3 + H_2O \rightarrow 2\ Ag + 2\ HX + H_2SO_4$
Fixation	$2\ Na_2S_2O_3 + AgX \rightarrow Na_3[Ag(S_2O_3)_2] + NaX$
	$4\ KCN + 2\ AgX \rightarrow 2\ K[Ag(CN)_2] + 2\ KX$
Etching	$3\ Ag + NO_3^- + 6\ H^+ \rightarrow 3\ Ag^+ + 3\ H_2O + NO$

The common development procedure for daguerreotypes was the formation of Ag amalgam particles next to the latent image Ag clusters. Edmont Becquerel reported a development procedure based on AgI without the use of mercury in 1840, where AgI was converted to latent images (by the "Becquerel effect"). In the following year, in 1841, the Viennese Natterer brothers developed novel procedures representing a breakthrough photographic technique providing a hitherto unachieved high sensitivity due to various halogenide mixtures without Hg. This development technique could be reconstructed as the hydrolysis of S_2Cl_2 resulting in SO_2 and H_2SO_3 which acted as a reductant for the Ag halides leading to AgNPs around the latent image Ag nuclei. The authors also used S_2Br_2 instead of S_2Cl_2 and claimed a superb sensitivity. Josef Natterer performed the fixation of the developed image either by potassium cyanide, KCN, or by sodium thiosulphate, $Na_2S_2O_3$ which dissolved the remnant halides.

In the light-exposed area, a photon-catalysed reduction led to colloidal silver nanoparticles (AgNPs). The observed particle size distribution is between 30 nm and 120 nm. This is def-

initely less than Ag amalgam particle sizes typical for daguerreotype highlight image microstructures which are between 100 nm and 2.5 µm. The colloidal particles on the plate exhibited a conversion shell layer consisting of Ag_2O, Ag_2S, and some AgCl.

The etched plate surface corresponds to low light exposure in contrast to the high exposure area which does not exhibit etching features. The AgNPs and their conversion shells are practically absent in the midtone and dark tone areas. These, in contrast, are dominated by larger etching bits with diameters of 200 – 400 nm. Any conversion layers involving Cl or S are absent while Ag_2O layers are abundant.

Joseph Berres succeeded in developing an etching technique in 1840 for the common daguerreotypes involving Ag amalgams. Thus, enabled first reproductions of daguerreotypes. The exposed Hg/Ag areas showed a high resistance towards etching with nitric acid. The unreacted AgX could be attacked by the acid. Berres applied a gum arabic solution on the fixed image surface before the etching step. The gum arabic showed high wetting on the exposed AgNP regions and negligible on the unexposed bulk Ag regions. Thus, preferentially the later areas were etched. The formed depressions could accept the printing ink in the follow-up reproduction step. Berres further reproduced original etched photographs by a process in which an auxiliary intermediate film of Au was electroplated from $AuCl_3$, and numerous Cu replica could be generated by electrotyping. Thus, innumerable photographic reproductions were possible for the first time. One can assume that the unexposed areas of the investigated plate which did not exhibit any Hg content was treated in an analogous way.

Deterioration processes generally observed with common daguerreotypes which contain Hg are absent in the present case. Scratches, finger smudges and blurred areas visible as fine, dark and grey lines and spots are most probably old damages and may date back to the time of image production. Remnants of splashes may have been caused unintendedly during the etching process.

4.12. Experimental Section

A systematic materials analysis of the daguerreotype plate showing the Joseph II's equestrian monument on Josefsplatz in Vienna (Fig. 18 left) has been undertaken. An average Ag-layer thickness was evaluated by x-ray fluorescence (XRF; Roentgenanalytik Systeme GmbH & Co. KG, maXXi 5/PIN). Optical micrographs of the surface topography were recorded with a digital microscope (Keyence, VHX-5000) together with the z-scan techniques. Scanning

electron microscopy (SEM) was combined with energy-dispersive X-ray spectroscopy (EDX; QUANTA FEG 250, FEI). The topography was imaged with secondary electron signals. Since secondary electrons are emitted from very close to the specimen surface very high-resolution images could be achieved. The composition was analysed with energy-dispersive X-ray spectroscopy (EDX).

4.13. Conclusion

Joseph Berres (1796-1844), who was the first to succeed in etching the heliogravures for intaglio printing and thus for reproducible photographic illustration, was probably involved in the production of the investigated plate. Joseph (1819-1862) and Johann (1821-1900) Natterer were medical students working together with their colleague Erwin Waidele on new photochemical sensitization methods for the daguerreotype. They recognized the advantages of bromine and chlorine over iodine and experimented with several different sensitization processes. In 1841, using Josef Petzval's new lens, they succeeded in taking some of the earliest known photographs of street scenes with people. It can be assumed that the young medical students worked closely with the anatomy professor Joseph Berres. The detection of chlorine in the absence of mercury on the surface of the photo proves this assumption.

Acknowledgements

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III. Physicochemical characterization of electrodeposited printing plates from the early 1840s in Vienna

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Contributions:
The concept for this publication originates from my study of electroplated printing plates. I developed the theory and carried out optical microscopic examinations. W. Kautek and I planned further investigations with NHTC, Romania, and carried out the data evaluation. ATR-FTIR spectroscopy and multispectral imaging were performed by I. M. Cortea, L. Ratoiu and R. Rãdvan at NHTC, Romania. GC-MS was performed at KHM, Vienna.

Keywords: electrotyping, intaglio printing, reproduction, surface morphology, colophony

4.14. Abstract

The technology of electrotyping was successfully applied for the reproduction of printing plates shortly after its invention in 1838. In Austria, high-quality printing plates have already been produced at the beginning of the 1840s in the first laboratory for electrotyping in Vienna. However, little is known about the properties of electrodeposited printing plates from this early period. In this study the manufacturing process, surface structure, chemical composition, and corrosion properties of three electrotype plates from the Viennese laboratory were investigated. Two samples were intaglio plates made for printing and one was a relief negative for electrotyping reproduction. They exhibited no metal coating, whereas the third sample, a relief plate, was coated with silver to ease the separation from an electrotype copy. Thin colophony films with traces of vegetable wax were identified by ATR-FTIR spectroscopy and GC-MS. Multispectral imaging analysis by UV reflectance indicated a strong inhomogeneous distribution between elevations and depressions of the relief plate.

4.15. Introduction

Electrochemical metal deposition can be applied as electroplating or electrotyping (galvanoplasty, electroforming) [1]. The latter is an electrochemical method for forming metal parts that exactly reproduce a model [10,12–15]. The inventor of this process was the German physicist Moritz Hermann von Jacobi who reported his invention in St. Petersburg in 1838 [2] and published his experiments in a brochure entitled "Galvanoplastik" in 1840 [37].

Electrotyping was adopted for the reproduction of intaglio images from the beginning as a novel reproduction technology for graphic arts where copper reproductions of engraved metal plates were generated [8,11,24,36,60,63,76]. Until then, only a limited number of prints from the original engraving plate could be realized. Particularly in intaglio printing, the lifespan of the plate was limited because the quality decreased by mechanical wear. The invention of electrotyping served to overcome this limitation. Electrotyping allowed to produce any number of electrotype duplicates from the original engraving plate, and therefore an unlimited number of prints [63]. The impact of this new technology on the dissemination of art was compared with the invention of printing in 15th century, and its potential of spreading knowledge [8,24,43]. In 19th century, graphic art became increasingly popular (“graphics boom”). This boosted the development of new reproduction techniques as e.g. electrotyping. The value of limiting the size of an edition and of including the volume of the edition in the print number (e.g., "35/90" for the 35th print in a total edition of 90) was recognized not until ca. 1880. It became common that artists signed

their print in pencil and numbered it to show the uniqueness of that impression and the total edition size [43].

In electrotyping, a galvanic positive copy ("Basrelief, Matrize") [4] was generated from the original engraving which again was used as master relief for a further electrodeposition step leading to the final printing plate ("Matrize") [4]. The original copper engraving ("Urtypus") was not used for printing production and therefore, suffered no mechanical wear. Moreover, the final printing plate ("Matrize") was more hard-wearing than the original because it exhibited a much denser metallurgical structure than the engraving ("Urtypus") which was based on a rolled copper sheet. This could theoretically extend the number of prints indefinitely.

A diluted sulfuric acid (H_2SO_4) solution saturated with copper sulphate ($CuSO_4$) served as electrolyte [6,13,17–19]. Sometimes zinc sulphate ($ZnSO_4$) was added to this solution in order to reduce the brittleness of the deposited copper [76]. The original engraving ("Urtypus") as well as the galvanic positive copy ("Basrelief, Matrize") were cleaned before they were introduced into the galvanic bath. A reported version was a treatment with turpentine and ethyl alcohol followed by diluted nitric acid (HNO_3) [76]. Another report describes the cleaning by a caustic potash (KOH) solution and a treatment with greases or oils, such as olive oil, which was mechanically reduced by paper wiping and brushing [4,56]. This was the prerequisite for the separation of the copy from the master plate. An alternative to this grease and oil overlay was the electroless or galvanic silver deposition based on a cementation reaction between the copper substrate and a AgCl/NaCl solution [76]. The losses of copper metal were so low that no quality change was observed.

Shortly after the invention of electrotyping it was rapidly developed to an unrivalled quality at the first Austrian laboratory for electrotyping established and run by Franz Theyer and Erwin Waidele in Vienna from 1841 on [8,19,24,27,31,33,34,42,58,71,75,134–136]. More than 70 partly silver or gold-plated copper electrotyped artefacts were rediscovered in the collection of the Technisches Museum Wien, Austria [75]. They provide an important information on the structure of depressions in various intaglio-printing techniques. However, the knowledge concerning the production of early electrotype artefacts for graphic arts is still very restricted. Solely general information can be found in early publications and technical encyclopaedia from the 19th century [11–13]. Since then, no scientific investigation of the used materials and techniques has been undertaken.

In the present study, investigations of the surface film nature and morphology of three electrotype plates manufactured in 1844 in Austria were performed. Conclusions were drawn in respect to the manufacturing and deterioration processes, as well as possible conservation treatments.

Fig. 27 Electrotype engraving copper plates (a-c) and print (d). “St. Joseph”, 1843, Vienna. Technisches Museum Wien, 23 × 30 cm. (a) intaglio plate (Inv.Nr.: 84183/1), (b) intaglio plate (Inv.Nr.: 84183/2), (c) relief plate, (Inv.Nr.: 84183/3), (d) print from plate 2 (Inv.Nr.: BPA-015565-10).

4.16. Material and methods

The three electrotype plates (Fig. 27 and 28) of interest were manufactured in 1844 by the first commercial laboratory for electrotyping in Austria, established and run by Franz Theyer in the period 1839–1851 [8,19,24,27,31,33,34,42,58,71,75,134–136]. From Theyer's collection, one silver covered electrotype plate "Hl. Joseph" (Technisches Museum Wien, Austria, Inv.Nr.: 84183/3) was chosen for a chemical surface investigation (Fig. 27c). The following text is engraved below the image: "St. Joseph, der du auf Erden den Herrn der Herrschenden Dir unterthänig gesehen hast, bitte für uns! Jos. Führich m.v. Leop. Beyer sculpt".

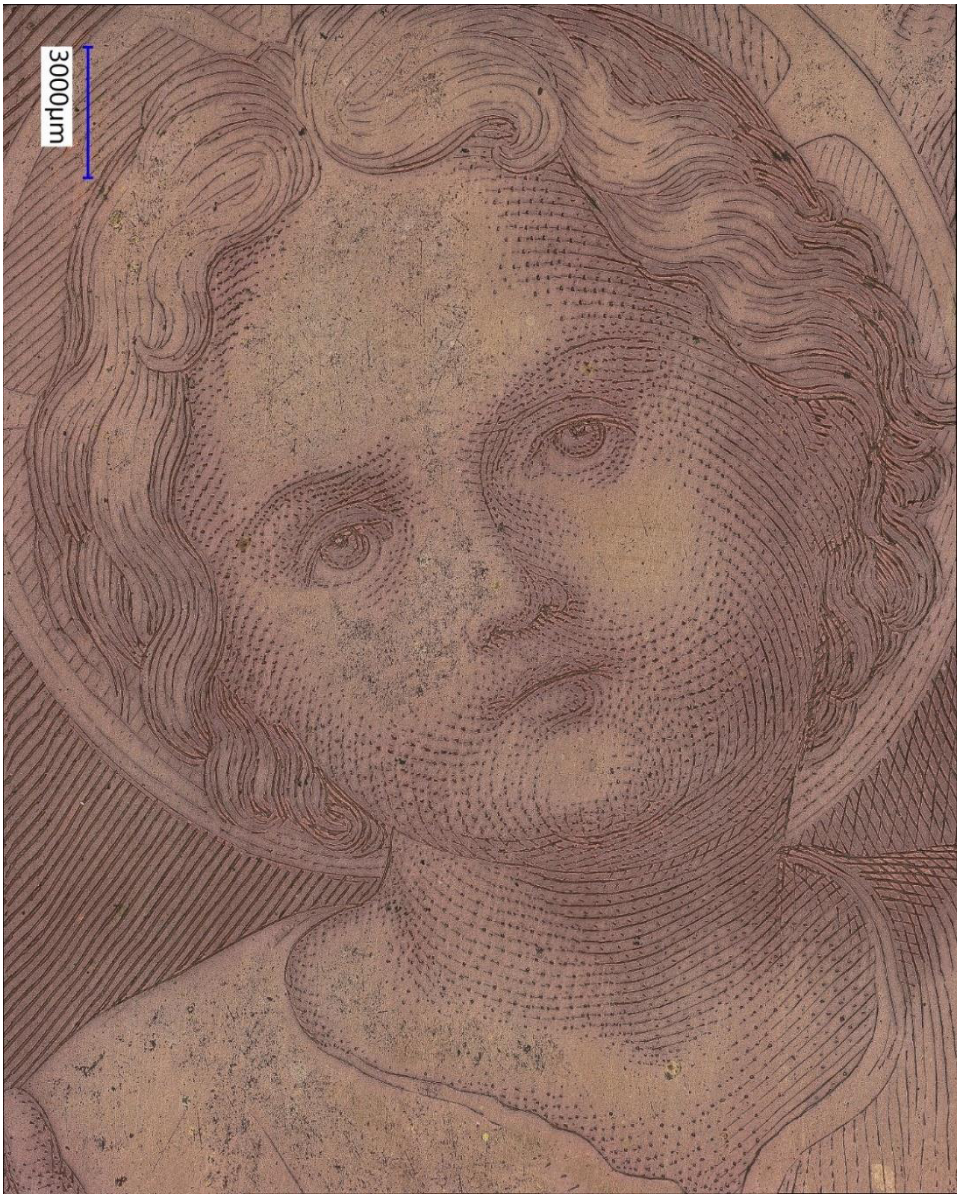

Fig. 28 Microscopy image (z-scan) of a detail of the electrotype engraving relief plate in Fig. 1c. "St. Joseph", 1843, Vienna. Technisches Museum Wien, 23 × 30 cm. plate (Inv.Nr.: 84183/3).

The analysis options were very limited due to the size of the objects (Table 9). No destructive methods were chosen [45,46,137]. Morphological investigations were performed by optical microscopy (z-scans; Keyence, VHX-5000). Scanning electron microscopy (SEM) and energy-dispersive x-ray fluorescence spectroscopy (EDX) were not accessible due to the size of the object. Ultraviolet, visible and infrared reflection, but also visible fluorescence imaging investigations in the spectral range from 320 nm to 1550 nm were undertaken by a multi-spectral imaging system (MuSIS 2007, Art Innovation, Hengelo, The Netherlands) to identify the surface distribution of any organic coatings [138]. Six imaging modes could be employed: visible, infrared in three bands (700 nm - 1550 nm), false-colour infrared, fluorescence, and ultraviolet (365 nm). The ultraviolet imaging mode provided a sensitive tool to detect organic thin films. A black light UV lamp (100 W, 365 nm, Hg I-line) was utilized as source. In the visible recording mode, two halogen tungsten lamps were placed at 45 degrees in respect to the sample surface. The plate was mounted on a black canvas background with the aim of reducing stray light scattering.

Table 9. Electrotype plates. “St. Joseph”, 1844, Vienna. Technisches Museum Wien.

Description	Inv.Nr.	Historical labelling on the wrapping paper in the archive	Dimensions [mm]
Intaglio plate	84183/1	„St. Joseph, der du auf Erden den Herrn der Herrschenden Dir unterthänig gesehen hast, bitte für uns! Jos. Führich m.v. Leop. Beyer sculpt.“	224×309×1
Intaglio plate	84183/2	"Druckplatte der hl. Josef - gestoch. v. Beyer. Mit der Aufschrift aus Theyers Laborat. 844 Den 27 April 40 Drucke Original“	224×309×1
Relief plate	84183/3	"Der hl. Joseph nach Führich gest. v. Beyer Reliefplatte"	225×298×2

The quantification of silver film thickness of silver covered electrotype plate (Technisches Museum Wien, Austria, Inv.Nr.: 84183/3, Fig. 27c) by x-ray fluorescence spectrometry (XRF; Röntgenanalytik Messtechnik GmbH, maXXi 5 PIN) was not successful. Values were below the detection limit.

The chemical nature of surface films was analysed by means of GC-MS analysis and attenuated total reflectance FT-IR spectroscopy. The GC-MS analysis (Agilent Technologies, USA, 6890N gas chromatograph connected to a quadrupole mass spectrometer, model 5973N) of the resinous binding media was based on the esterification of resinous acids followed by the identification of particular resins according to their resinous acid methyl esters.

Infrared spectroscopy is a powerful tool in heritage science [37]. The attenuated total reflectance FT-IR spectroscopy (PerkinElmer, Spectrum Two FT-IR Spectrometer, designed for large specimen equipped with an ATR accessory, GaldiATR PIKE) was performed in the wavelength range between 4000-400 cm-1. Eight scans and a spectral resolution of 4 cm-1 were chosen. The spectral processing was done by applying a baseline correction and a smoothing factor for noise reduction (PerkinElmer Spectrum software). FTIR signals were observed on multiple spots. Selected waxes, oils, and varnishes served as reference samples.

4.17. Results and Discussion

These three electrotype plates (Fig. 27) show the high-quality standards of the Thayer's laboratory [8,24,26,139]. This can be particularly observed in a detail example (Fig. 28). The first two plates, Fig. 1a and 1b, exhibit a warm orange tone and high gloss. Rims, ~1 cm from the edges, appear filed and polished. The surfaces of all three plates show numerous scratches, which exhibit local corrosion products in contrast to the rest that preserved the bright colour and mirror-like gloss.

An optical microscopic profile evaluation allowed the identification of the first two plates as intaglio engravings (Fig. 27a and 27b), and the third silver–plated as an electrotyped relief [56] (Fig. 27c). The grooves of the intaglio plates (comp. Fig. 27a and 27b) exhibit depths up ca. 40µm (Fig. 29a and 29b). The elevations of the electrotyped relief (comp. Fig. 27c) show heights of up to ca. 40 µm (Fig. 29c).

Multispectral imaging analysis provided convincing results by UV reflectance and VIS imaging (Fig. 30). A low UV reflectance indicates a strong absorption on high relief areas, whereas a high UV reflectance a low absorption

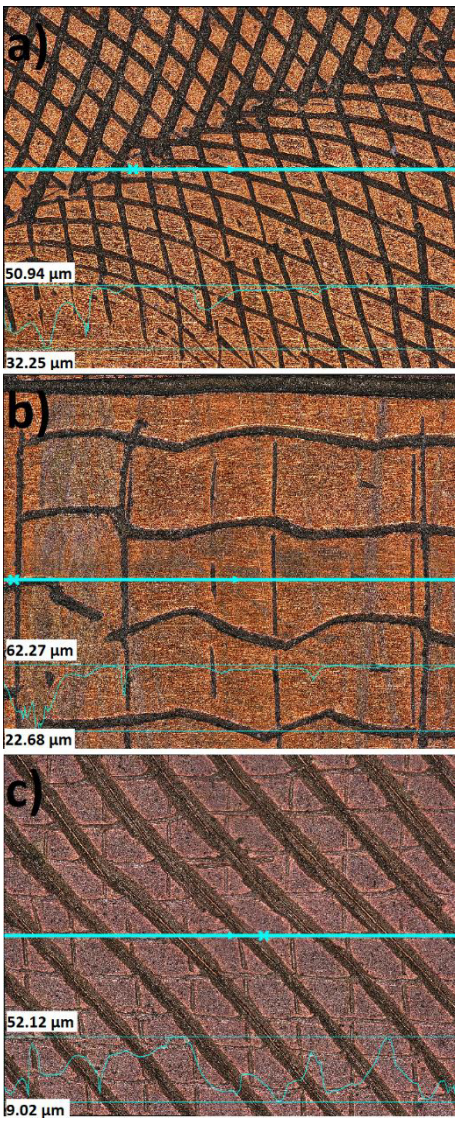

Fig. 29 Optical micrographs with profilometry showing typical profile lines. Electrotype engraving copper plates "St. Joseph", 1843, Vienna. Technisches Museum Wien. (a) intaglio plate (Inv.Nr.: 84183/1), (b) intaglio plate (Inv.Nr.: 84183/2), (c) relief plate (Inv.Nr.: 84183/3).

on depression areas. That means that an organic film (see below) is distributed inhomogeneously on the sample. Obviously, the film application reached preferentially the high relief areas. Horizontal scratches appear light indicating low UV absorption and thus a missing (removed) organic film. They are not observable in the VIS image demonstrating that they belong to a distinct layer different from the metal plate. These mechanical damages were probably introduced during the storage period.

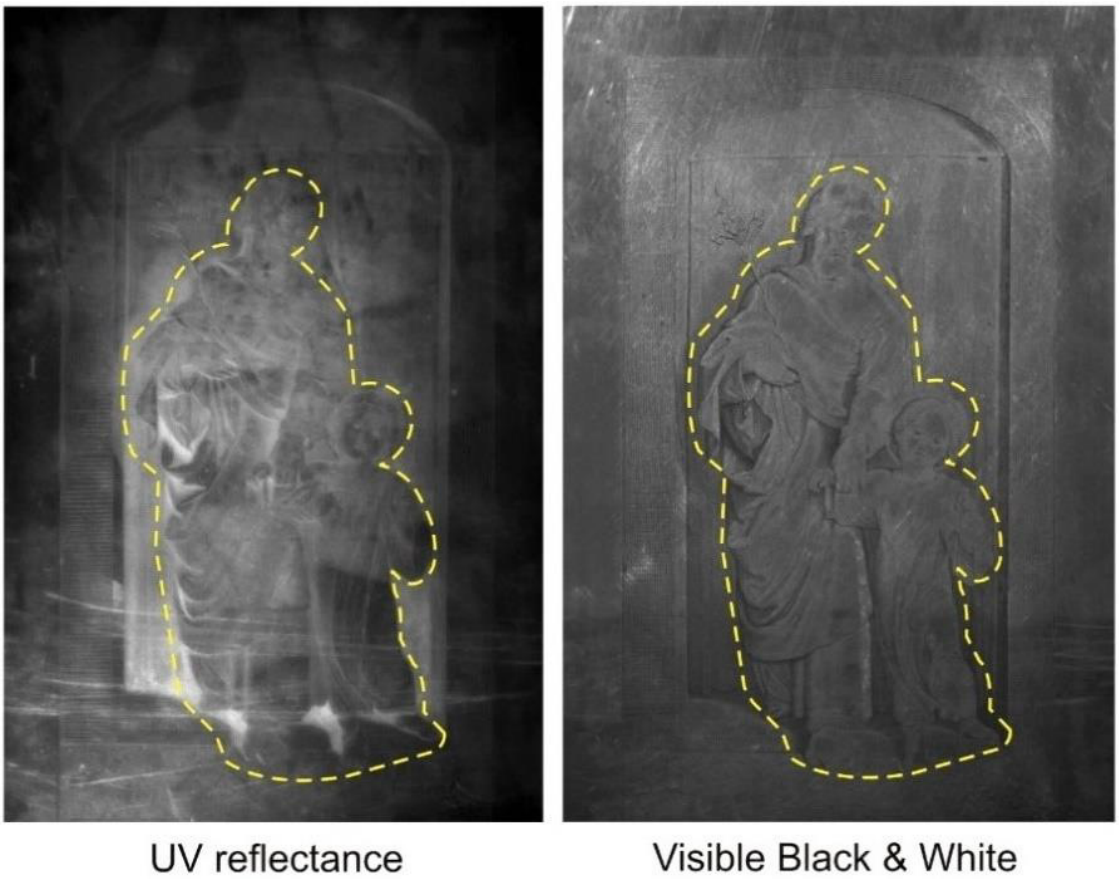

Fig. 30 Multispectral imaging analysis of the electrotype engraving intaglio plate "St. Joseph", 1843, Vienna. Technisches Museum Wien (Inv.Nr.: 84183/2). UV reflectance image and black and white photography.

The plates were analysed by ATR-FTIR in order to identify organic coatings. As reference served a copper plate covered with a native oxide layer exhibiting a characteristic Cu_2O (cuprous oxide) vibration around 620 cm^{-1} (Fig. 31, Table 10). This peak was considered as a reference for the coated originals. The carbonyl region (1800-1550 cm-1) and the fingerprint region (1550-500 cm-1) were evaluated. Resins, varnishes and vegetable wax coated on Cu plates served as IR reference samples (Table 2). The C-H vibration bands between 600 and 1450 cm-1 were compared with the data of various natural varnishes. The strong C=C bands at 1520-1540 cm-1 and

1610-1650 cm-1 of the intaglio and the relief plate could not be observed with the copal, dammar and linseed oil samples, butt correlated with colophony. The absorption bands at 600-640 cm-1 in the fingerprint region due to C-H rocking vibrations indicate hydrocarbon waxes or colophony [140–143]. A C=O band around 1700 cm-1 are practically absent indicating low oxidation. Colophony ages by thermal, biological and photo degradation resulting in the aromatization of unsaturated cycles and hydroxylations [143]. This could be monitored by FTIR.

Table 10 ATR-FTIR results of an intaglio plate (Inv.Nr.: 84183/2) and an electrotype engraving relief plate (Inv.Nr.: 84183/3). "St. Joseph", 1844, Vienna. Technisches Museum Wien. Fingerprint bands [cm^{-1}] in comparison with those of natural varnishes and vegetable wax.

Intaglio	**Relief**	**Colophony** [42]	**Copal**	**Dammar**	**Linseed Oil**	**Wax**	**Bonds**
640 (s)	600-640 (s)	652			680	635	CH_x
	800						
	880	910		880 (s)			
	980	980	970 (s)	980		950	
1120 (s)	1110 (s)	1107	1080	1100	1080	1070 (s)	
			1140 (s)	1160 (s)	1160 (s)		
1230	1230	1239	1220 (s)		1220	1250	
1400 (s)	1410 (s)	1365	1380 (s)	1380 (s)	1370	1360	
	1450 (s)	1450	1450 (s)	1440 (s)	1450(s)	1460	
1520 (s)	1540 (s)	1496					C=C
1640 (s)	1610-1650 (s)	1610–1615				1640 (s)	C=C stretch
		1697	1710 (s)	1700 (s)	1720 (s)	1730	C=O

Wax and colophony can efficiently protect copper from corrosion [82,100,137]. Such a coating is practically irreversible applied to a cleaned metal and may have a long-term protective action in repetitive printing steps and in storage. Before the introduction of synthetic lacquers in the 1900s, colophony was commonly used alone or in mixtures with e.g. wax or linseed oil as surface protection for musical instruments, furniture, paintings and in arts and crafts [144]. Colophony was also often applied in certain manufacturing processes as a recess lacquer or cover lacquer. It has long been used extensively in lithography and, in general, for objects that have been partially etched. In the 19th and 20th centuries this covering method was also used in the production of patterned sheet metal, which was often provided with a fine decoration by the transfer printing process [52].

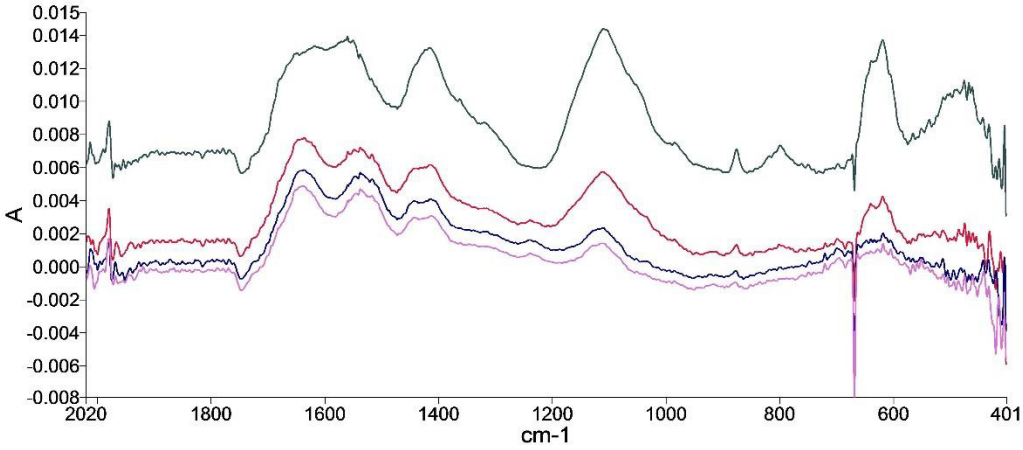

Fig. 31 ATR-FTIR spectra of the electrotype engraving relief plate "St. Joseph", 1843, Vienna. Technisches Museum Wien (Inv.Nr.: 84183/3).

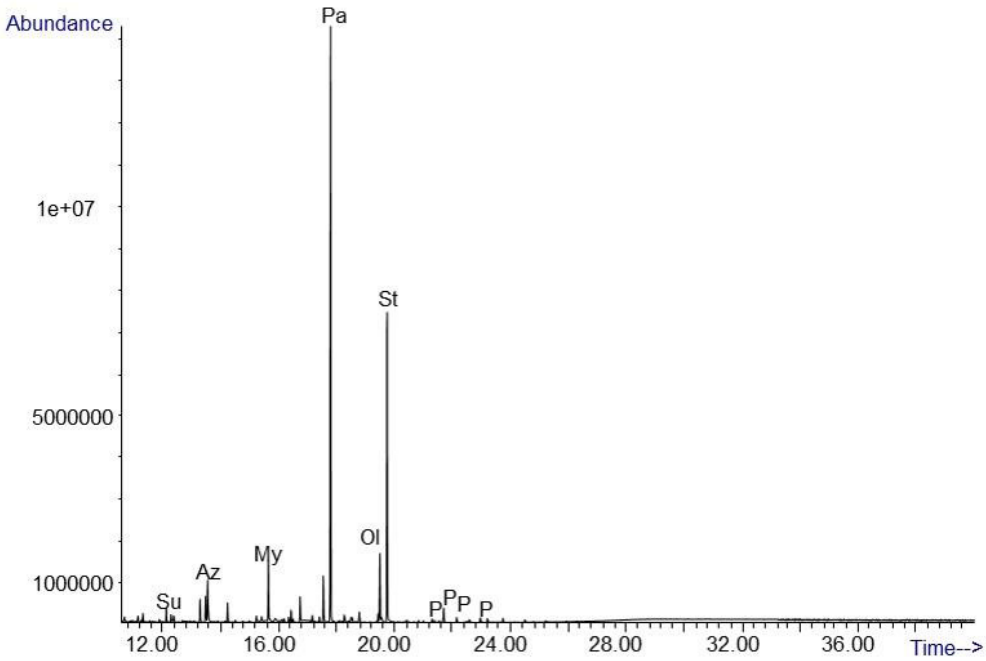

Fig. 32 Chromatogram of the coating material on an electrotype intaglio plate. "St. Joseph", 1843, Vienna, Technisches Museum Wien (Inv.Nr.: 84183/2). Su: suberic acid. Az: azelaic acid. My: myristic acid. Pa: palmitic acid. Ol: oleic acid. St: stearic acid. P: diterpenes of pine resin (Pinus species).

A further analysis of the coating on the intaglio plate (Inv.Nr.: 84183/2) was performed by GC-MS [141]. The coating material was taken from the surface by a cotton swab wetted in a solvent mixture (EtOH:i-octane, 1:4). The extract was then evaporated, and the solid residues analysed. The sample is composed of a series of fatty acids and traces of pine resin such as colophony [143]

(Fig. 32). This is in accordance with the ATR-FTIR results (Table 10). In comparison to the chromatogram of cotton swab blank sample, the intensities of fatty acids, namely palmitic acid and stearic acids (Pa, St) are higher, what could suggest that fatty acids are not only remnants from the cotton swab, but they are also from some additional fat impurities caused by the handling of the metal plate. The presence of an oil-resinous coating (dicarboxylic acids, Su, Az) in minute amounts overlapped with the signal of the fat impurities.

4.18. Conclusions

A physicochemical characterization of the manufacturing processes, the surface structure, the chemical composition, and the corrosion properties of three electrotype plates with the same motif of St. Joseph manufactured by the Laboratory of Franz Theyer and Erwin Waidele in Vienna, Austria, was performed. The surface micro-morphology revealed that two samples were intaglio made for printing and one represented a relief negative for electrotyping reproduction. The intaglio types showed no metal coating, whereas the relief plate was covered with silver to enable an easy separation from an electrotype copy. Thin organic films were identified as mainly colophony with traces of vegetable wax by ATR-FTIR spectroscopy and GC-MS. However, an exact assignment of the colophony wax coating and its significance on the electrochemically deposited printing plates could not be clearly assigned. It is quite conceivable that this coating played a role in the manufacturing process, but it also might be applied as surface protection.

The depths of the intaglio grooves and the elevations of the electrotyped relief (comp. Fig. 27c) were up to 40 µm. Multispectral imaging analysis by UV reflectance indicated a strong absorption on high relief areas. Obviously, an organic film was applied solely on the elevations not reaching the depressions. Scratches on all samples were probably introduced during the storage period.

With this study providing new information on the electrochemical reproduction of original printing plates, an identification of graphic prints and the elucidation of the 19th century's printing techniques may be facilitated.

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servation science and archaeology“, RO07/2012, in the frame of the "Scientific and Technological Cooperation Austria - Romania" by the OeAD (Austrian Agency for International Mobility and Cooperation in Education, Science and Research).

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Partial support by the project „LIST - In-situ laser diagnostics in conservation science and archaeology “, RO07/2012, in the frame of the "Scientific and Technological Cooperation Austria - Romania" by the OeAD (Austrian Agency for International Mobility and Cooperation in Education, Science and Research).

5. Ongoing research to be published

5.1. Evaluation of techniques in "Franz Theyer's galvanoplastisch-artistischen Laboratorium" in Vienna of 1840's

The metal objects distinguish themselves in size, form, the nature of the materials used and the quality of execution. Approximately one third of the artefacts possesses a gold or silver coating. It is an interesting fact that, while some of the examined objects had distinct silver coatings over their entire surfaces, only some thin and almost invisible traces of silver could be found on others. Silver deposits vary in thickness to some extent creating a painterly and almost three-dimensional effect. The various thicknesses of the silver deposits result in the reddish copper shining through to a greater or lesser degree, which influences not only the color but also lends a photographic appearance (Fig. 33).

Fig. 33 (a) rolled copper plate, silver-plated and treated with roulette; (b) electrotype copy from A; (c) print on paper. © Technisches Museum Wien

The investigation of surface morphology using optical and scanning electron microscopy revealed completely different surface structures. On some plates a very coarse structure can be seen in the depressions of a motif, while in others it is rather fibrous (Fig. 35, 36). In contrast, the depressions of the motif on some plates are extremely flat and porous and differ from the denser structure of the surroundings (Fig. 34). This testifies to Theyer's and Waidele's experimentation to achieve a perfect replica of historical graphic techniques.

It is evident that when painting the pictures in the technique of galvanography [11,32,33,36,55,57,60,63,74–76], the colors were always individually mixed. Probably the artists themselves made their colours according to their own grinding style and the imitated technique. In the galvanic cavities, the granularity of the paint can be clearly seen, since sometimes pigments of different fineness were mixed into the paint. In order to create a coarser structure, sometimes fine ground rosin or other substances were sprinkled onto the still moist paint [59,74].

In the case of very porous structures, it is assumed that the image motif was etched into a smooth galvanically produced plate. In an article of the Polytechnical Institute, it is reported that Theyer succeeded in electroforming drawings on paper made with his specially designed electro-ink (Elektrotinte) [9]. Since the historical writing source does not provide any details on the technique and the preparation of the paper, nothing is known about this process so far. With optical and scanning electron microscopy, however, very fibrous motifs could also be detected (Fig. 35, 36). In addition, fine brush strokes can be seen on the plates. These originate from the application of the conductive silver or graphite layer (Fig. 37).

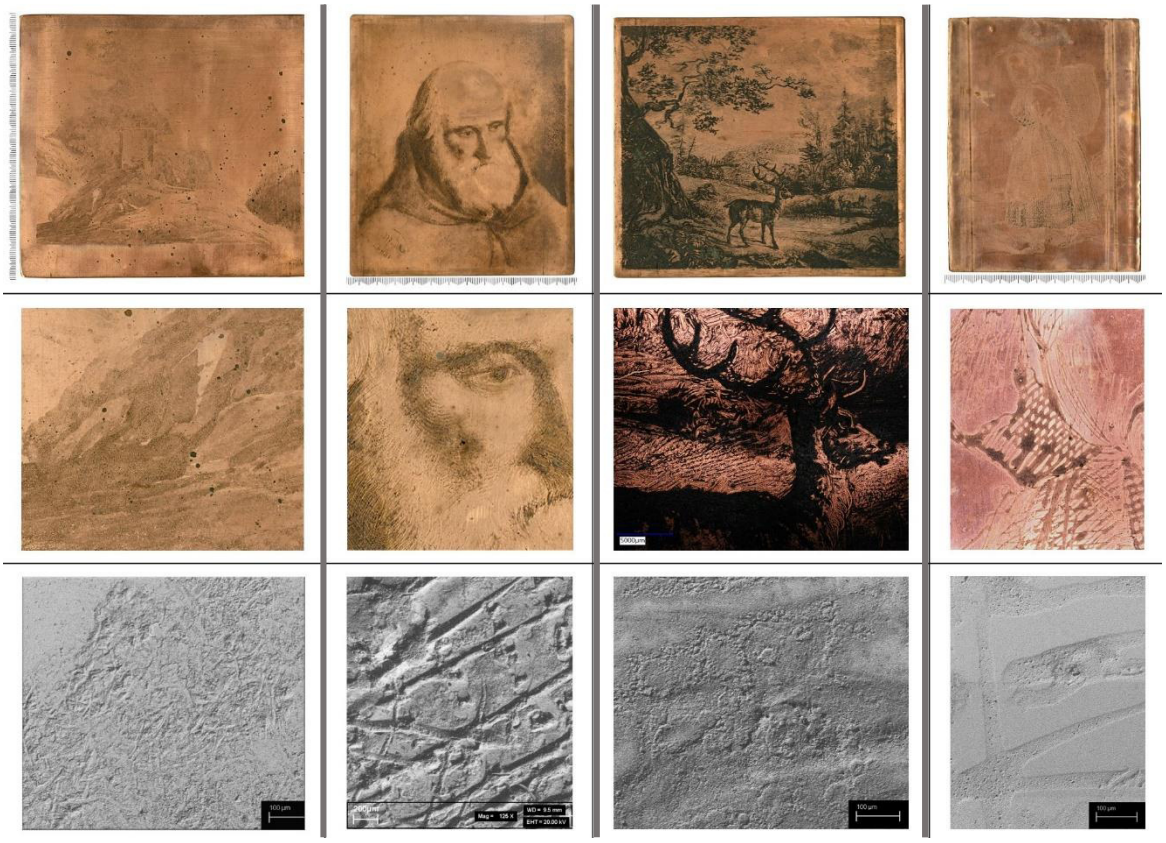


Fig. 34 Four examples of printing plates made by electrochemical deposition with their very specific surface

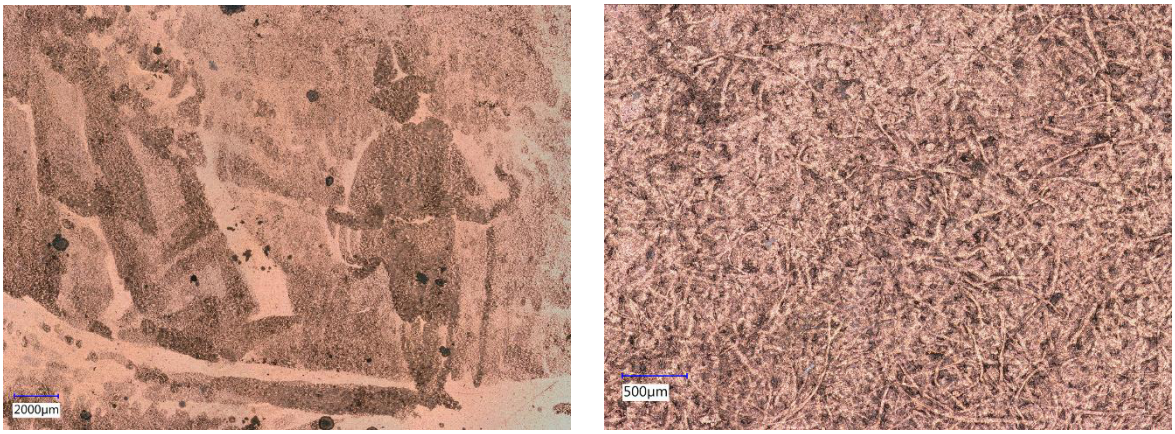


Fig. 35 Fibrous structure in the depressions of the plate Inv.Nr.:83939/4

Fig. 36 Fibrous structure in the depressions of the plate Inv.Nr.:83939/13

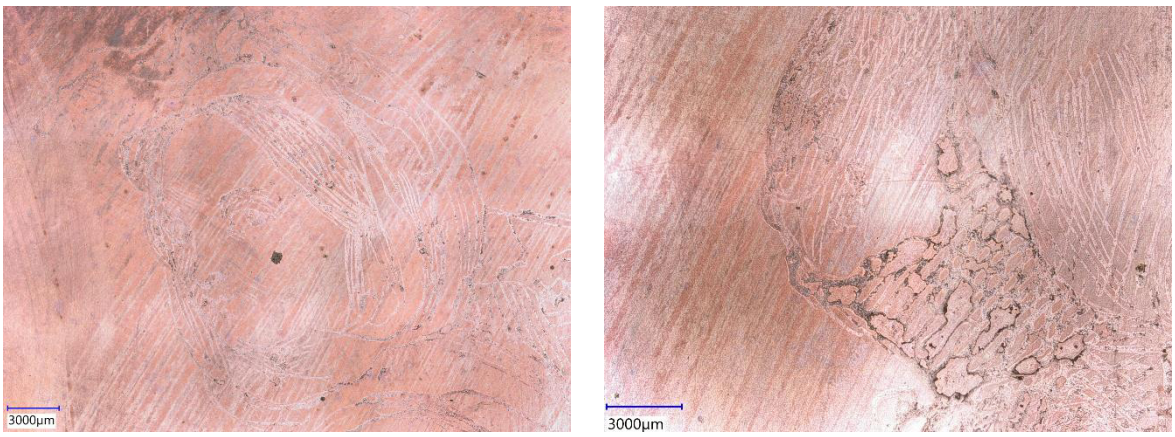


Fig. 37 Fine brush strokes on the plate Inv.Nr.:83939/7

The use of multiple manufacturing techniques has been demonstrated on many panels. Traces of tools such as dry needles, roulette and various hallmarks could be detected microscopically (Fig. 38).

Fig. 38 Visible marks of several tools on the plate Inv.Nr.:83939/11

Physical-chemical investigations by SEM/EDX of the silver and copper surfaces have provided information about the morphology and chemical composition. Based on these investigations, some clearer information about the manufacturing process of the objects were obtained. A number of typical production characteristics were identified on printing plates making it possible to distinguish various used techniques. Examination of the surface profilometry enabeled to differentiate the printing plates from the relief (negative) plates.

Special attention was paid to the silver plating of metal objects from the Theyer's laboratory (Fig. 39). There are two reasons for this:

I. The silver coatings are in a very good state of preservation and show hardly any oxide or corrosion formation. This inertness of the silver reaction is very untypical, especially when one considers that the stock was in a wooden cabinet for decades and wood is known to cause rapid oxidation of the metals due to the acid cleavage. Usually, an unprotected silver-plating leads to a rapid reaction with the surrounding air and the associated oxide and sulphide formation influences the aesthetics and durability of the object.

II. Visible silver plating, and sometimes only silver traces, can be found on most of the plates in the picture area. With some plates, however, they are predominantly found outside the image area.

Fig. 39 (a) rolled copper plate, silver-plated and treated with roulette, Inv.Nr.:83939/7; (b) electrotype copy from A, Inv.Nr.:83939/8; (c) print on paper. © Technisches Museum Wien

The thickness of the metal coating on all the electrotype objects with silver or gold deposits was investigated using X-ray fluorescence analysis (XRF). In order to compile information on the homogeneity and to obtain reproducible values, the thickness (*d*) of the metal coatings were measured in several areas, and a mean value was calculated. The lowest measurable *d* was 0.03 µm. Optical micrographs of various regions off the plates provided a detailed picture of a partial coverage with a silver film in the depressions and on the plateaus. Although

silver particles were detectable by EDX and visually distinguishable, they were not allways measurable by XRF on every plate due to the marginal thickness of the coating.

A substantial number of the artefacts exhibit various surface alterations resulting both from previous use and inadequate storage: from slight soiling and tarnishing to severe staining and corrosion or color splashes. However, it is remarkable that most of the galvanographic objects in this collection are only lightly stained or tarnished. This lack of chemical reaction displayed by the silver is very untypical, especially when one considers that the collection was housed in a wooden cupboard for a long time and acidity from wood is known to cause the rapid oxidation of metals [77]. The first assessment of the gold-coated medallions showed a correlation between the amount of corrosion and the thickness of the gold coating. In generall, it was also possible to observe a relation between the level of corrosion and the degree of sheen or roughness on the surface (Fig. 40).

Fig. 40. Left: galvanoplastic: electrodeposited Au on Cu; middle: galvanoplastic: electrodeposited Cu; c: galvanoplastic: electrodeposited Ag on Cu. © Technisches Msueum Wien

Energy-dispersive X-ray spectroscopy (EDX) confirmed, besides dirt, the presence of residues of printer's ink and often traces of silver (1 per cent), mainly detected in the depressions of the galvanographs. These components can be attributed to the process of making the painted areas conductive by scattering them with powdered silver. Remains of the electro ink can in some cases be seen on the top of the surface or in the motiv depressions (Fig. 41, 42), mainly of the relief (negative). It could not be confirmed if some plates posess rests of electro ink because they vere directly painted with this medium.

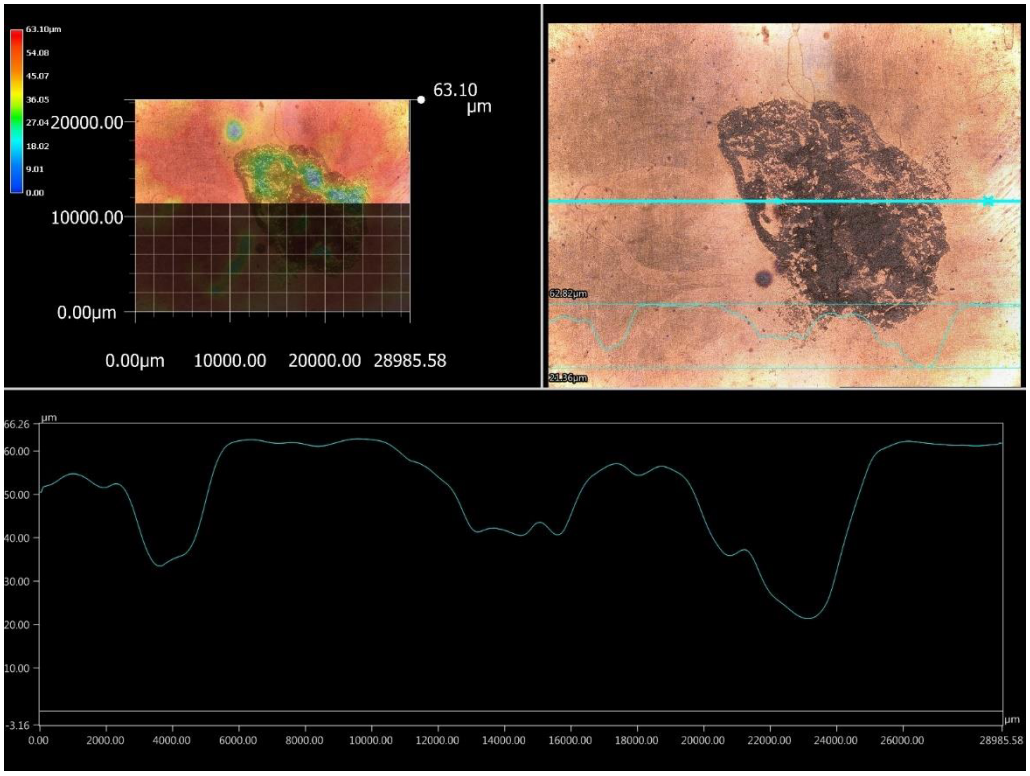


Fig 41. Optical profilometry of the surface structure from the plate Inv.Nr.:83939/3 probably with dark leftovers from the historical color ink “Elektrotinte”.

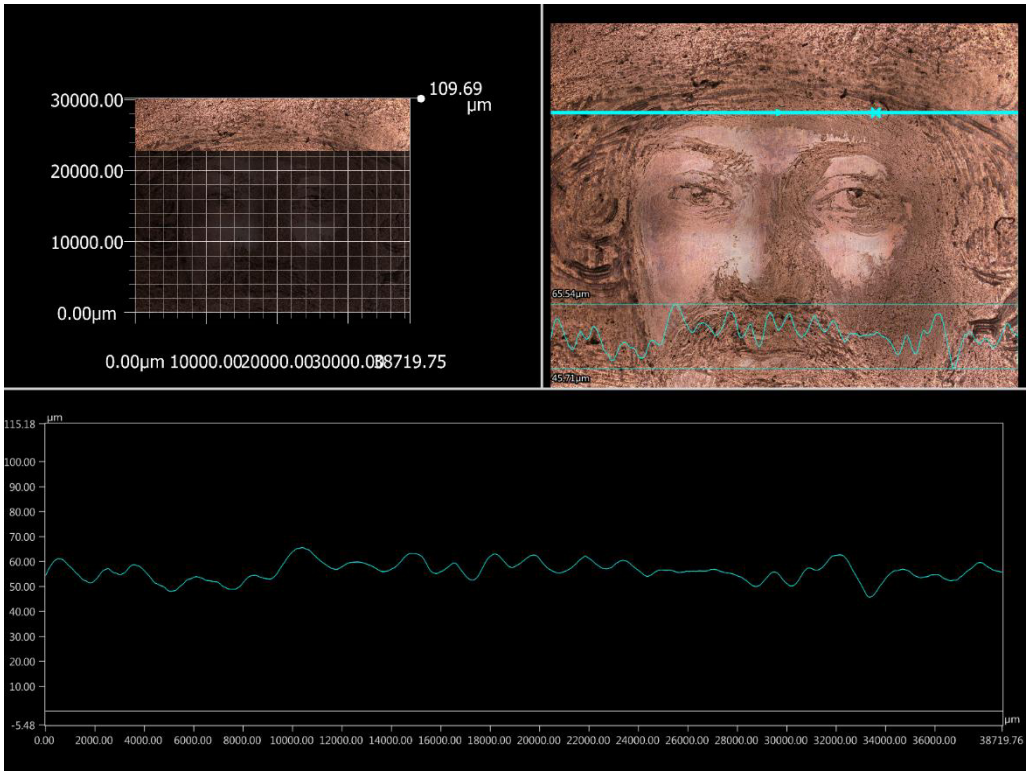


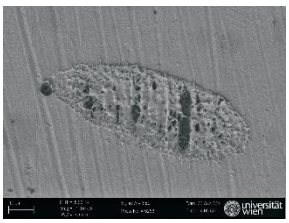
Fig 42. Optical profilometry of the surface structure from the plate Inv.Nr.:83939/1, probably with dark leftovers from the historical color ink “Elektrotinte”.

5.2. LIBS depth profile of Au on Cu models

With the aim of developing a less invasive method for the analysis and detection of thin metal coatings Laser-Induced Breakdown Spectroscopy (LIBS) promises to be a successful approach [145–149]. Based on recent LIBS-developments in the Department of Physical Chemistry of the University Vienna [150–152], preliminary depth profiles, layer thickness measurements and elemental analyses were performed with this technique on a dummy object resembling the objects in Theyer's collection.

In addition to the light microscope, morphological changes on the surface of the samples were investigated with a scanning electron microscope (SEM). The SEM evaluations allowed more detailed morphological infirmation, particularly at parameters where crater depths could not be measured. In these cases, nonetheless, modifications in the form of the increase of roughness could be observed. These phenomena represent the basis of the above quantified incubation behaviour. Increased roughness led to increased net absorption and thus to substantial lower ablation thresholds than with smooth surfaces.

Table 11. Laser ablation craters after LIBS depth profiling of a gold-plated copper sheet. F = 3.5 J/cm². Number of pulses: N.

$N = 1$	
$N = 2$	
$N = 5$	
$N = 10$	

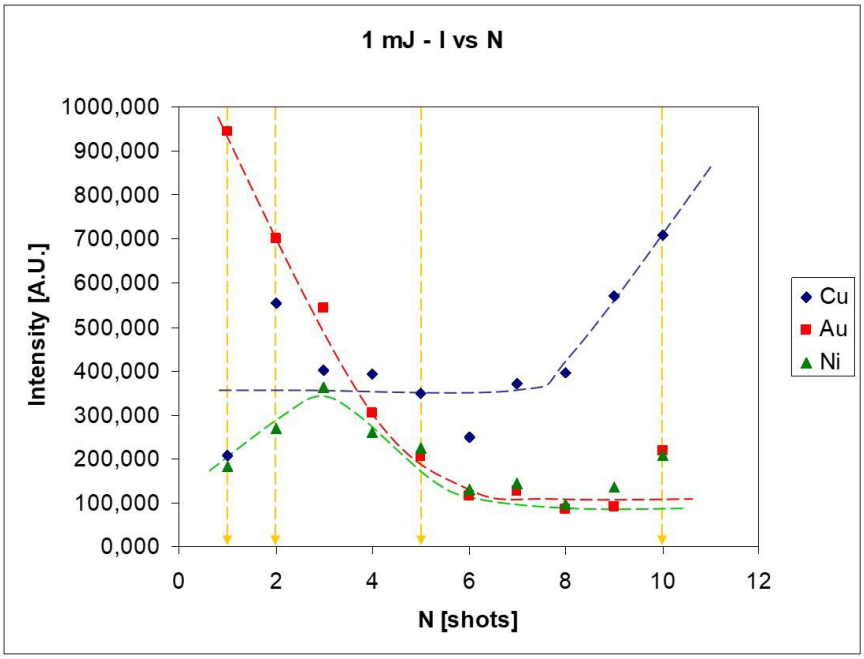
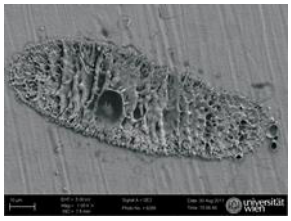
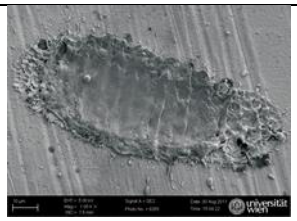
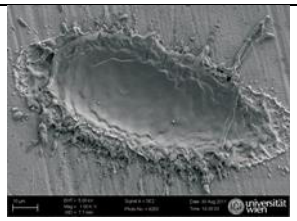
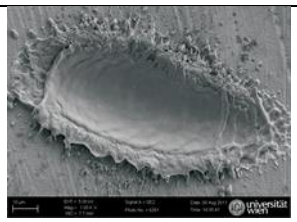


Fig. 43 LIBS depth profile of a gold-plated copper sheet. F = 3.5 J/cm², d = 1.1 µm/pulse

Table 12. Laser ablation craters after LIBS depth profiling of a gold-plated copper sheet. F = 8.7 J/cm². Number of pulses: N.

$N = 1$	
$N = 2$	
$N = 5$	
$N = 10$	

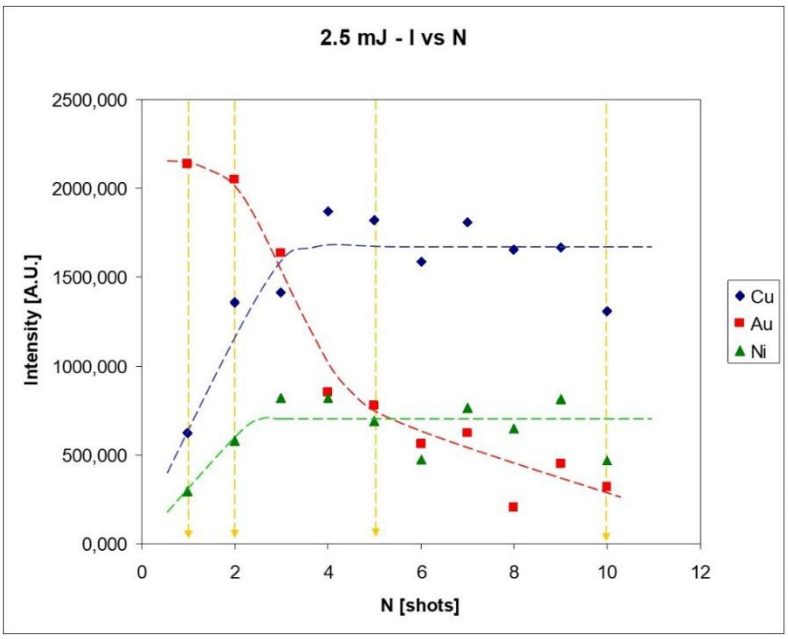


Fig. 44 Laser ablation craters after LIBS depth profiling of a gold-plated copper sheet. F = 8.7 J/cm². Number of pulses: N.

LIBS on model coating systems showed that depth profiles are only feasable with coating systems above ca. 1 µm per layer (Fig. 43 and 44). LIBS depth profiles depend strongly on applied fluences. SEM images reveal overlapping melt and splash phases at the crater edges (Table 11 and 12). This causes precision losses in the resolution of burried interfaces. LIBS test at low fluences, F = 3.5 J/cm², on ultra thin Au coating on original Au on Cu galvanoplastic did not result in sufficient sensitivity for the thin Au film. EDX however shows low depth resolution (most signal from bulk and organic contamination), but sufficient sensitivity for the ultra thin film.

5.2.1. Longterm Corrosive Behaviour after LIBS Treatment of Au on Cu model

A preliminary investigation of the longterm corrosive behaviour after LIBS treatment resulted in the observation of the corrosive conversion of redeposited material (here Cu substrate material) in the form of vapour redeposition or splashing. The problem of local galvanic corrosion induced by such foreign phases, but also the opening of the base material by the laser ablation appears as a decisive issue for the application of LIBS on coated metal artifacts (Fig. 45).

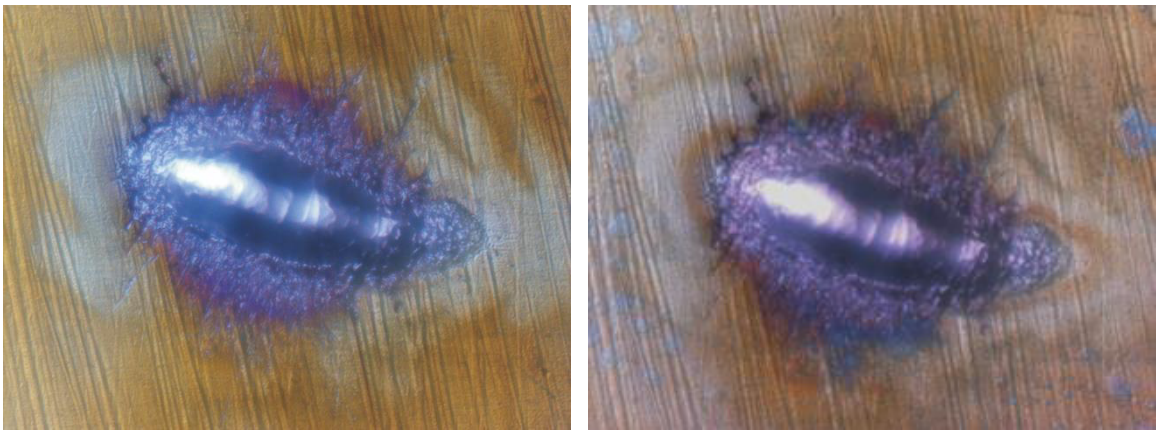


Fig. 45 left: Z-Scan Image of LIBS crater on Au on Cu model. F = 17.5 J/cm², N = 5. right: Z-Scan Image of LIBS crater on Au on Cu model. F = 17.5 J/cm², N = 5 After corrosion test, 2 weeks, 25 °C, 100% RH

5.3. Production of galvanographic models

A total of six sample plates were prepared and painted (two made of bare copper and 4 of silver-plated copper). The colour mixtures used were based on historical literature [24,57,139,153] and applied in different pastosities and compositions (Fig. 46). The six plates were mounted individually on an acrylic glass plate and the space between the acrylic glass plate and the copper plate was sealed with liquid wax to prevent the electrolyte from penetrating between them. The copper plates were electrically contacted by means of an insulated copper wire. These wires were also used as a mechanical suspension device for the acrylic supports including the copper plates in the electrolyte bath. An additional silver lacquer contact electrode was applied along the circumference of the samples.

Fig. 46 Six painted dummies bevor the electrochemical deposition

The six prepared samples were immersed in a sulphuric acid thick-film copper bath (Bright Copper ACG 8, Schlötter Galvanotechnik) at 20°C (Table 13). According to the manufacturer, the copper bath contains an additive for brightness and leveling, but the chemical identity of the additive is unknown. The bath was kept in constant motion by a pump. A direct current supply (Heraeus, 10V, 100A) served as the current source for the electrolysis. The

copper anodes (200x400 mm, 1 cm thick) were covered with polypropylene anode bags. A voltage of 0.5 V was applied until the entire sample area was overgrown. The voltage was then increased to 2V. After this electroplating process, the deposited copper plates were separated from the underlying positive plate with a blunt knife. The newly formed copper plate, the negative, was rinsed with water and polished with a soft brass wire brush as described in the historical reports [12,13,15,52].

Table 13 Galvanic bath "Glanzkupferbad ACG 8"

Parameter	Information provided by manufacturer
Cu concentration	39,0 gl^{-1}
H_2SO_4 concentration	97,8 gl^{-1}
Cl^- concentration	58,0 g^{-1}
Fe concentration	0,1 gl^{-1}

The electrochemical experiments were carried out in a two-electrode drop cell. The reference electrode was an Ag/AgCl (RE, + 0.222 V vs. SHE) and as a counter electrode a gold wire spiral (CE) in a glass tube with a porous frit as electrolyte transition was used. Cyclic voltammetry and open circuit transient measurements were performed with an electrochemical workstation (CH Instruments, 760C). The electrolyte was a 0.1 M K2CO3 (pH = 10.6) solution with deionized water (Milli-Q). The pH value was determined using a glass membrane electrode (Metrohm, 780 pH Meter). Before starting the electrochemical measurements, the plate within the measuring window was degreased by wiping with a cotton swab soaked in acetone.

Optical microscope images were taken with a digital microscope (Keyence, VHX-5000).

The painting medium applied to the plates should establish the conductive electrode for the galvanic deposition of the copper layers. The experiment has shown that the morphology, i.e. the granularity and pastiness, the thickness of the applied paint and, in particular, the separating layer used, have an influence on the quality of the new electrodeposited copper layer. This series of experiments has shown visible similarities with the original plates from the laboratory of Theyer & Waidele. In particular, the transfer of the conductive Ag layer to the electroplated copy of the painted plate was clearly confirmed (Fig. 47). Further aspects such as the influence of the conductive layer on the roughness of the surface (Fig. 48) and its long-

term corrosion behaviour are discussed in more detail in the publication “Duplication of Uniqueness: Electrotyping in Nature Printing and its Application in Contemporary Art”.

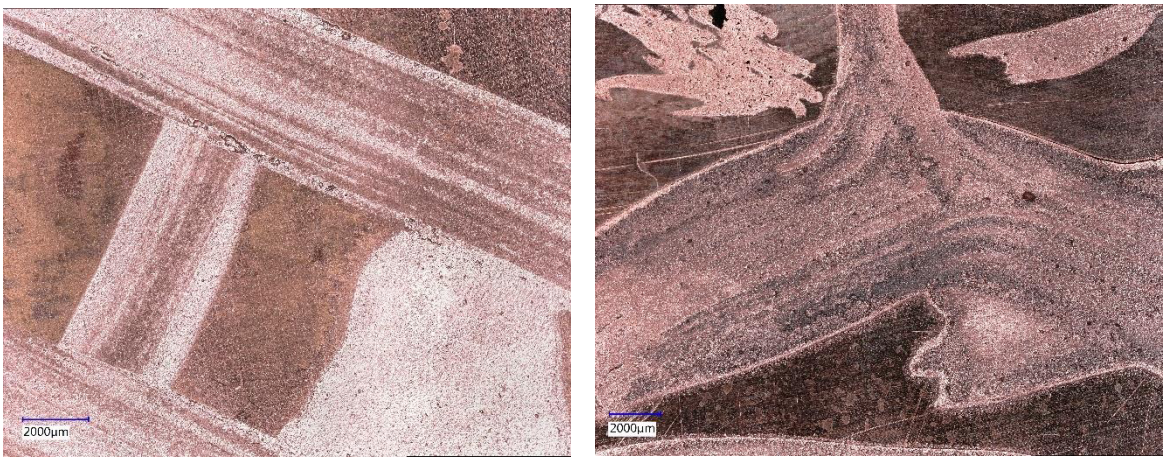


Fig. 47 Typical structures on the front side of generated electrotypes

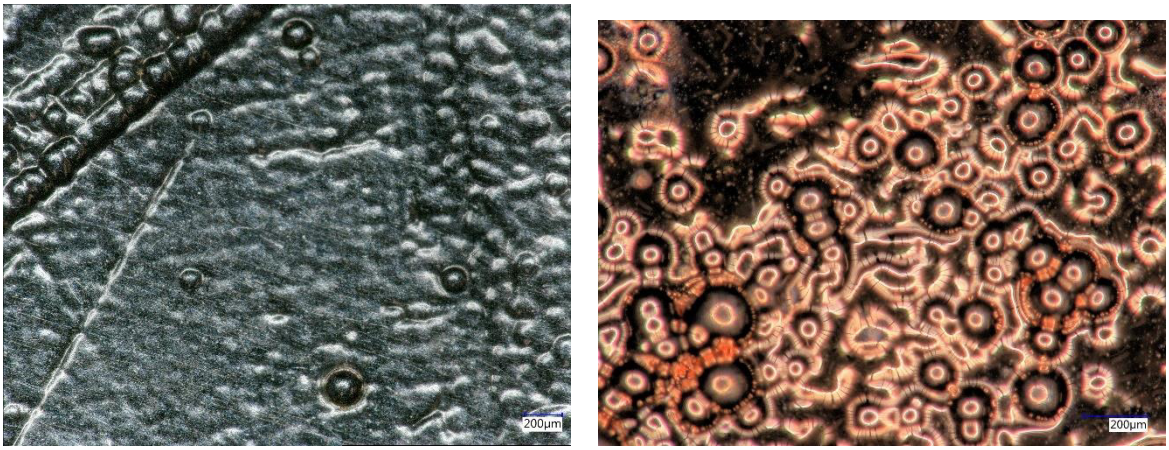
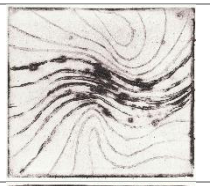
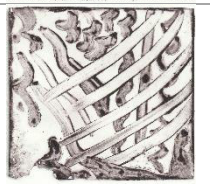
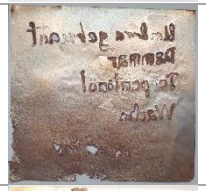
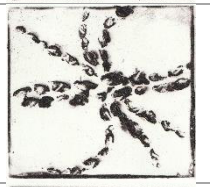
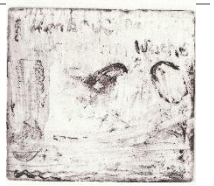


Fig. 48 Typical structures on the back side of generated electrotypes

Table 14 Overview table with the technical details and pictures of painted plates, the generated electroforms and the prints on paper made with them

Nr.	Plate preparation	Components of the paint	Colour consistency	Characterization	Painted plate	Electroformed layer	Printing on paper
G01	Copper plate silver plated and iodized	Vine black pigment, dammar varnish, siccative	High viscosity	Complete, compact layer, good faithfulness to the original			
G02	Copper plate silver plated and iodized	Graphite powder, vine black pigment, oil of turpentine, siccative	Low viscosity	Incomplete but compact layer, good faithfulness to the original			
G03	Copper plate silver plated and iodized	Graphite powder, vine black pigment, oil of turpentine, siccative	Medium viscosity	Incomplete but compact layer, great faithfulness to the original			
G04	Copper plate silver plated and iodized	Burnt umber pigment, dammar varnish, oil of turpentine, wax, siccative	Medium viscosity	Incomplete, uneven, inhomogeneous layer, good faithfulness to the original			
G05	Pure copper plate with a wax separating layer	Vine black pigment, dammar varnish, siccative	High viscosity	Complete, compact layer, good faithfulness to the original			
G06	Pure copper plate with a wax separating layer	Burnt umber pigment, dammar varnish, oil of turpentine, wax, siccative	Medium viscosity	Complete, compact layer, bad faithfulness to the original			

5.4. Comparison and characterization of prints

- **5.4.1. Ferdinand's Bridge in Vienna (Die Ferdinandsbrücke) before August 1840**

Among the art prints found in the collection of Franz Theyer, particularly one photographic print has attracted our attention. It turned out that it was produced by an etched daguerreotype with the photographic motive of the Ferdinand's Bridge in Vienna (1840) (Fig. 49 upper left) [113]. Through intensive research for the origin, four additional prints of the same motif were found. The prints of this etched daguerreotype ("heliograph") photographed by an unknown author and etched by Josef Berres are reported in the possession of the British Library, London, Helfried Seemann Collection, Vienna (Fig. 49 upper right) [35], the Albertina, Vienna (Fig. 6 bottom left), the and at the George Eastman Museum, Rochester (Fig. 49 bottom right).

All five prints were cut to different sizes and sometimes odd. The edge marks of the printing plate are only visible on the print from the George Eastman Museum (Fig. 49 bottom right). The three prints, from the British Library [35], the Albertina (Fig. 49 bottom left), and the George Eastman Museum (Fig. 49 bottom right) have had their skies shortened considerably. They also have the same shady spots in the upper left corner caused by deformation or insufficient thickness of the printing plate (possibly the low thickness of the plates helped to reduce the costs). Despite the differences in the grey tones, these three prints contain numerous fine line marks. Obviously, the printing plate was either scratched and damaged in the printing process, or it was not well polished initially during the plate preparation for the daguerreotype process.

The print from Theyer's cabinet (Fig. 49 upper left) and from the Helfried Seemann Collection (Fig. 49 upper rigt) differ from the other three above-mentioned prints significantly. A big and immediately noticeable difference is that the contours of the roofs and the bridge come out much more precisely. There are also no shady spots in the upper left corner of the sky. These two prints contain two striking white areas - the sky at the top and the bright and flawless bridge wall at the bottom. These areas were reworked and smoothed on the printing plate, but not on the print. Scratches in the rest of the image are noticeable and were not smoothened in order not to lose photographic details. For Theyer's and Seemann's print, the printing plate was possibly brand new and not worn at all. More likely, however, is that a

reworked electroplated copy of this early etched daguerreotype made in 1840 was produced. The electrotype served for printing these two images and, with its robust material properties, helped to increase the print run immensely.

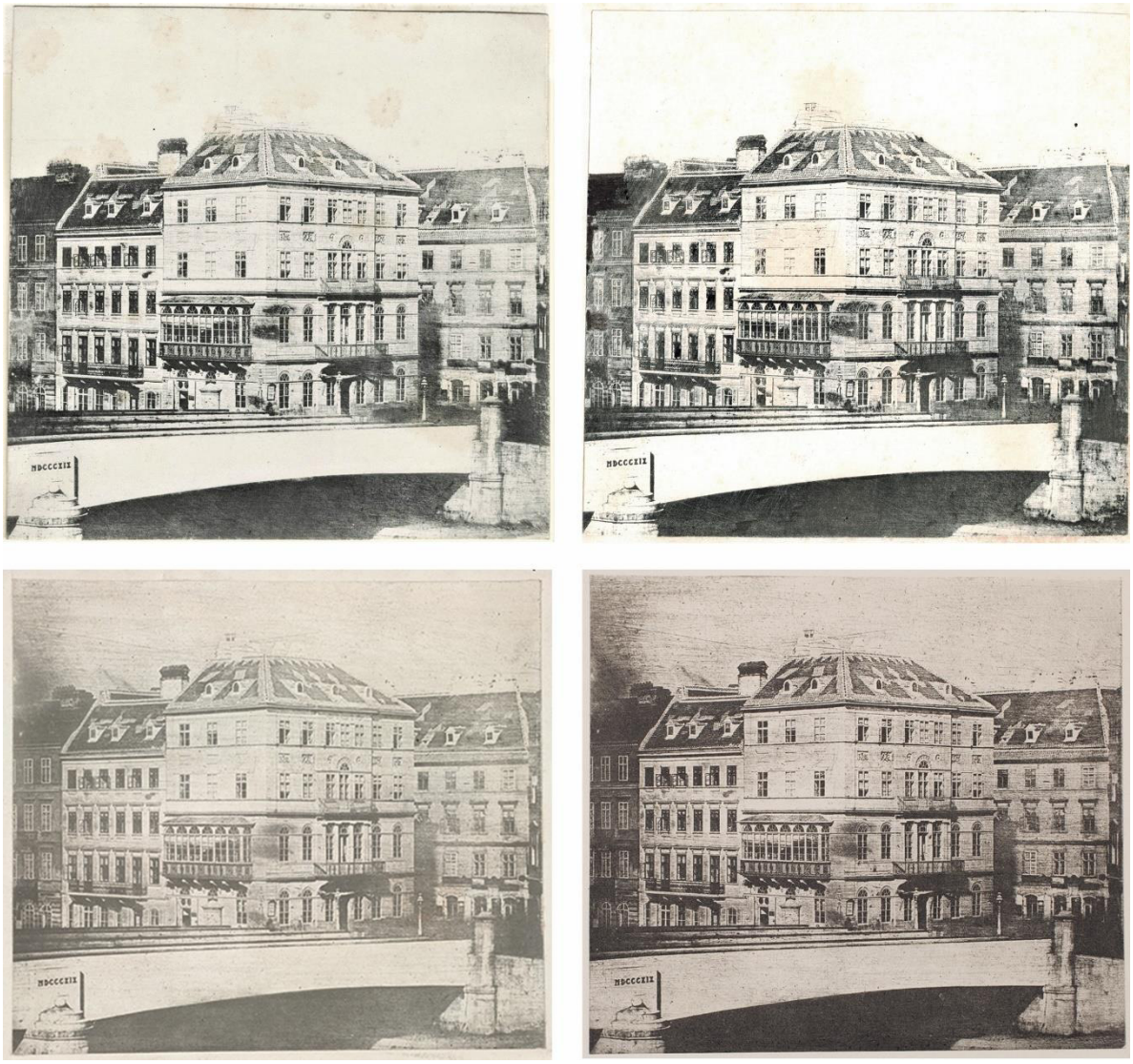


Fig. 49 Ferdinand's Bridge in Vienna 1840, Joseph Berres, print from etched daguerreotype. Upper left: Technisches Museum Wien, Vienna, Austria, BPA-015565-05_32, image size: 117 × 120 mm. Upper right: Helfried Seemann Collection, Vienna, Austria; inscribed: Nach der Natur, image size: 115 × 120 mm. Bottom left: Albertina, Vienna, Austria, FotoGLV2000/1717, inscribed: Die Ferdinandsbrücke, image size: 108 × 122 mm. Bottom right: George Eastman Museum, Rochester, NY, 1980.0276.0001, inscribed: Heliogravure auf geätzter Daguerreotypplatte von Joseph Berres 1840, image size: 110 × 124 mm (Courtesy of the George Eastman Museum).

- **5.4.2. Joseph II's equestrian monument on Josefsplatz in Vienna**

One other daguerreotype plate showing the Joseph II's equestrian monument on Josefsplatz in Vienna (Fig. 50), was also rediscovered in the same wooden cabinet like the print of the Ferdinand's Bridge [75]. This plate turned out to be a photograph on a metal plate in contrast to the other printing plates produced by electrotyping. It was not manufactured by electrodeposition because the reverse side do not exhibit a granular surface typical for electrochemical deposition.

Four prints from this scene are known today: three in the possession of the Moravská Gallery v Brně, Brno (Fig. 50 upper left, bottom left and right) and one at the Albertina, Vienna (Fig. 50 upper right). When comparing the plate (Fig. 50) with the four prints, differences are noticeable. All rounded upper window frames of the upper floor are visible on the plate but are missing on the prints. Complimentary to this, the lower steps at the bottom are missing on the plate but not on the prints. This may indicate that more than one, slightly shifted photographs were taken. In addition, the deeper tone of the monument is conspicuous on the prints. On closer inspection, the prints look like a collage consisting of two layers - the delicate background with the architecture facade and the equestrian monument in the foreground. Possibly, only the areas of the equestrian monument, including the stone pedestal decorated with reliefs and the pilasters bordering the monument, were reworked and etched deeper than the rest. It is obvious that the pavement was reworked as well, because it was not reproduced well on the photographic image (Fig. 50).

Despite the etched surface and various signs of aging, the plate retained its depth of field, the metallic brilliance and excellent image quality (Fig. 50 right). It is not known whether the plate was smudged during the manufacture and etching process, or at a later stage, due to inadequate storage and handling. The plate appeared yellow-brownish in the middle and blue-greyish at the blurry edges. Particularly the left edge of the plate and the pavement were strongly blurred. In addition, scratches, finger smudges and other blurred areas are visible as fine, dark and grey lines and spots on the plate. Due to the numerous grey scales and blurred areas, it was very difficult to distinguish between the physical damages and the chemical changes of the surface. Along the right side, approx. 15 mm from the edge, a dark stripe can be seen, which probably comes from the mechanical attachment in the electrochemical bath.

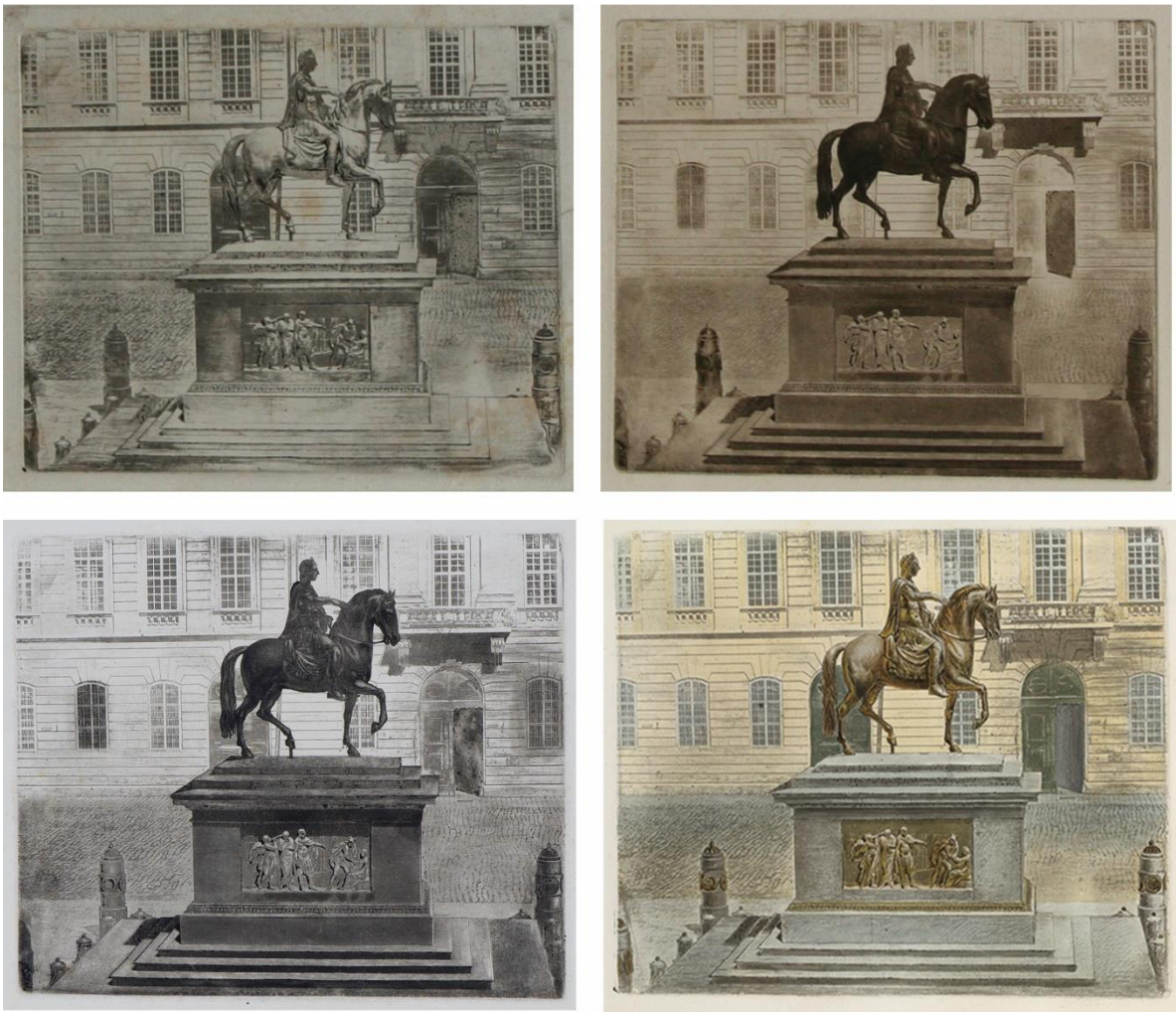


Fig. 50 Prints from etched daguerreotype. Josef Axmann, Joseph II's equestrian monument on Josefsplatz, Vienna, 1844. Upper left: Print on paper, Moravská galerie v Brně, Brno, Czech Republic, C2539, image size: 124 × 144 mm. Upper right: Print on paper, Moravská galerie v Brně, Brno, Czech Republic, C2476, image size: 123 × 145 mm. Bottom left: Print on paper, Moravská galerie v Brně, Brno, Czech Republic, C2540, image size: 123 × 145 mm. Bottom right: Print on paper painted in watercolours, Albertina, Vienna, Austria, DG18697, image size: 122 × 144 mm.

5.5. Electrochemical cleaning with an electrochemical pencil

The most common form of degradation observed on historic silver or silver alloy objects is the emergence of a dark layer of corrosion products [77,79,90]. This manifestation is referred to as tarnishing and is the result of the interaction of silver atoms on the surface with air pollutants such as hydrogen sulphide H_2S, carbonyl sulphide COS and other sulphur-containing organic compounds [154–158] in the atmosphere. The interaction yields silver sulphide Ag_2S, which is responsible for the dark colour of the tarnish film [159]. The corresponding reactions are:

$$2\ Ag + H_2S + ½\ O_2 \rightarrow Ag_2S + H_2O \tag{28}$$

$$2\ Ag + COS \rightarrow Ag_2S + CO \tag{29}$$

Tarnishing has the undesirable consequence of the formation of an unsightly dark layer on the surface of artefacts made from silver alloys. As a result, tarnish layers have a negative impact on the aesthetics [160] of historical silver artefacts and conservation professionals apply a variety of tarnish removal methods for their cleaning. Established methods [78,85,91,160,161] of tarnish treatment for the preservation of historical metallic artefacts include mechanical removal using abrasive pastes and tools as well as chemical removal using chemicals that effectively dissolve tarnish constituents, and finally electrochemical methods of which the electrolytic kind is the one being considered in this paper [79,89,90,162,163]. More seldom, laser [164,165] or plasma cleanings [166] are carried out.

The electrolytic treatment of tarnished artefacts with a pencil designed specifically for this purpose [89,90,162,163] is a more recently established method of tarnish removal. It is particularly well suited for the treatment of local corrosion outbursts and is a practical alternative to the electrochemical treatment of artefacts by immersion [18,88] in electrolyte. In the present work one such pencil is presented in a potentiostatic.

5.5.1. Methods of evaluation

The elemental composition of the formed tarnish layers was determined by energy dispersive X-ray spectroscopy (EDX), performed on a scanning electron microscope (SEM, Zeiss Supra 55 VP) in the Faculty Centre for Nano Structure Research of the University of Vienna. EDX

analysis was also used to assess the efficacy of the electrolytic pencil in the removal of sulphur from treated samples.

Surface morphology of both tarnished and treated samples was assessed through optical micrographs. Evidence for the effect of both contacting materials on sample surface was gathered. Optical microscopy (OM) was performed with an Olympus Measuring Microscope STM-MJS in the department of Physical Chemistry of the University of Vienna.

5.5.2. Electrolytic pencil

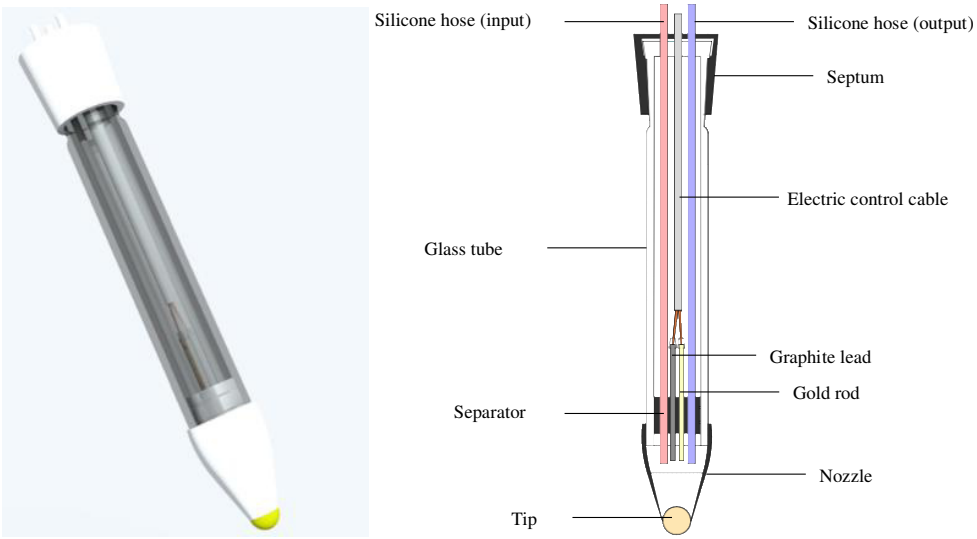


Fig. 51 Electrolytic pencil design (left) and cross section (right). RE: reference electrode. CE: counter electrode.

A customised electrolytic pencil for the potentiostatic treatment and analysis of metallic artefacts was designed, manufactured and developed (Fig. 51). It consists of a glass tube (l = 11 cm, internal diameter = 1.3 cm) with a tip mounting and a cap. The cap is composed of a rubber septum material and also served as a tubesheet. A gold rod (l = 4 cm, diameter = 1.5 mm) serves as counter electrode (CE). A graphite lead (l = 4 cm, diameter = 2 mm, Faber-Castell Fallmine TK 9071 3B) is used as a reference electrode (RE). These electrodes are separated and mounted by a polymeric tubesheet. Both the tubesheet and the tip mounting were manufactured by 3D print technology (Ultimaker2 3D printer and Ultimaker2 CPE printing material). The tubesheet is held in place inside the tube by two O-rings on either end. Two tip mountings with differently sized openings for the various diaphragm tips were manufactured. Electrolyte circulation to and from the electrolytic pencil is maintained by two

silicone hoses (external diameter = 3 mm). The counter and the reference electrodes are connected to insulated cables running alongside the silicone hoses.

The electrolyte was a buffered solution of 0.1 M $NaNO_3$. It was prepared by dissolving 10 g $NaNO_3$ in 1 l of distilled water and then adding 0.0136 g of tri-hydrated sodium acetate CH_3COONa and 0.1 ml of a 1 M acetic acid as an acetate buffer resulting a pH of 4.5. The three-electrode system was controlled by an electrochemical workstation (760C, CH Instruments). A peristaltic pump (Mini-S 420, Ismatec) provided the electrolyte circulation through the silicone hoses. The diaphragm tip material was varied. One was manufactured from a PVFM sponge (Polyvinylformal resin, AION Clean Room Sponge[1]), and the other was a polyester felt tip (for TIFOO GalvanoPen, MARAWE GmbH & Co. KG Donaustaufer Straße 378, D-93055 Regensburg).

Using the described pencil, electrolytic treatments were carried out with the main intention of assessing the suitability of the developed electrolytic pencil for the use in conservation practice. A test cleaning was carried out on an approximately 100-year-old, naturally tarnished pair of sugar tongs (Fig. 53 a), and a series of spot tests was performed on one approximately equally old, naturally tarnished Ag coin (Fig. 52). The effect of two contacting materials – pads made from a PVFM sponge and felt tips - on the sample surfaces and the effectiveness of treatments with regards to uniformity and homogeneity on various natural surface conditions were studied.

5.5.3. Treatment of a pair of silver sugar tongs

The selected, naturally tarnished pair of sugar tongs features a number of intricate ornamentations and reliefs as well as larger planes. Tarnish is especially severe within deeper lying regions in the vicinity of ornamentations. The object was degreased first by wiping it with a cotton swab imbibed with acetone. Electrical contact of the artefact was established with a crocodile clamp. The treatment process included an initial processing of the object in which the pad made from the AION Clean Room Sponge was used as contacting material. It was performed at -2.5 V vs. Graphite for 20 minutes and at -3 V vs. Graphite for 5 minutes. This was followed by the exchange of the nozzle with a bigger opening carrying the pad, for the

[1] Purchased from IAB Reinraum-Produkte GmbH, Erzberg 5, 38126 Braunschweig, June 2017

nozzle with a smaller opening. A felt tip was inserted and the treatment of the sugar tongs was resumed at -4 V vs. Graphite for 10 minutes. Table 15 summarizes the treatment procedure.

Table 15 Treatment parameters

Step	Intention	Tip material	Potential [V vs. Graphite]	Duration [min]
1	Overall reduction of tarnish on entire object	AION Clean Room Sponge	-2.5	20
2	Increase of potential to enhance reduction and remove persistent tarnish traces	AION Clean Room Sponge	-3	5
3	Targeted reduction of tarnish within deeper lying regions and overall enhancement of treatment outcome	Felt tip	-4	10

5.5.4. Spot tests

Localized spot tests were carried out on the unstamped reverse of a naturally tarnished Ag coin (Fig. 52). The potentiostat (760C, CH Instruments) was set to potential values ranging from -2 to -4.5 V vs. Graphite (steps: 0.5 V vs. Graphite). The electrolytic pencil was positioned on the coin and each potential was applied for 60 seconds. During spot treatments, the electrolytic pencil was moved using only slight circular motions to keep the spot size as small as possible. For each potential, a spot test was carried out once using a pad made from the AION Clean Room Sponge and again in a different place using a felt tip as contacting material in the nozzle of the pencil.

Fig. 52 Reverse of naturally tarnished Ag coin

5.5.5. Efficacy of the electrolytic pencil in conservation practice

From Fig. 53 B it is apparent that the treatment of the sample with the electrolytic pencil equipped with a sponge pad was insufficient. Mainly elevated features were subjected to reduction. Embossed areas remained dark and remaining tarnish traces were observed on the surface. The object also lacks the characteristic metallic lustre of silver and the achieved degree of brilliance is unsatisfactory. The sample exhibits a yellow tinge. After the additional electrolytic processing of the Ag sugar tongs with a felt tip (Fig. 53 C) the overall colour of the object is lighter and more uniform. Embossed elements and ornamentations could be reached and largely stripped of the tarnish film.

Fig. 53 State of the Ag sugar tongs before treatment A. State after treatment with AION Clean Room Sponge B and after treatment with felt tip C

EDX analysis (Fig. 54) performed after completion of the electrolytic treatment showed that both chlorine and sulphur were removed to a degree at which they were no longer detectable by this method. The elements detected include Ag, C, Cu and O. The removal of tarnish on the studied object was successful and confirmed the operational functionality and reliability of the electrolytic pencil. Nonetheless, the cleaning outcome was not entirely homogeneous and consistent. This can be attributed to the different thicknesses the tarnish layer presents throughout the surface of the object. Elevated areas were more exposed and lighter from the start due to the handling, in contrast to areas featuring reliefs and depressions, where a more persistent and thicker tarnish layer has formed over the decades.

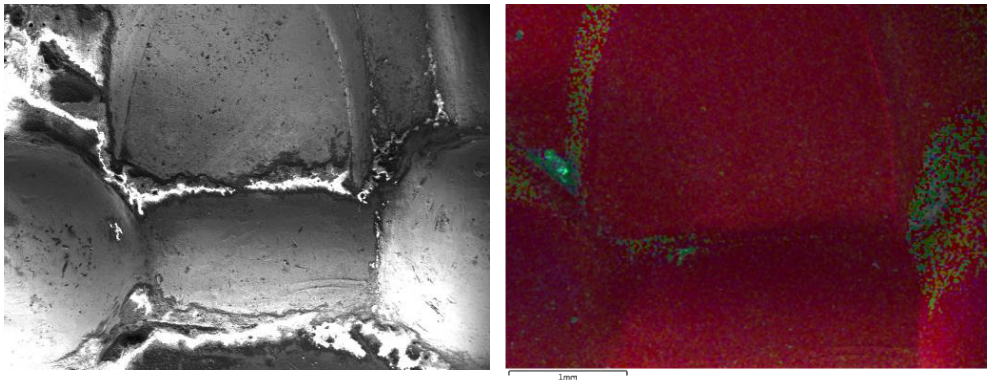


Fig. 54 Scanning electron micrograph of ornamental element in Ag sugar tongs (left) and EDX-analysis of elemental distribution in the same spot (right). Both micrographs were recorded after the completion of the electrolytic treatment. Red = Ag $L_{\alpha}1$, green = C $K_{\alpha}1_2$, violet = Cu $K_{\alpha}1$, turquoise = O $K_{\alpha}1$

5.5.6. Spot tests: Effect of the tip material

Generally, sites that were treated at stronger potentials (i.e. -3 to -4.5 V vs. Graphite) exhibit surfaces that are cleaner and lighter than those treated at weaker potentials, regardless of the material used as tip in the electrolytic pencil. This was to be expected, as the duration of the application of each potential remained constant. Greatest cleaning effects were achieved at -4.5 V vs. Graphite with the sponge pad and -3 V vs. Graphite with the felt tip. As the felt tip is noticeably firmer than the pad made from the AION Clean Room Sponge, this may be the consequence of an additional mechanical wear of the felt tip on the Ag surface. Spots cleaned with a felt tip at strongly negative potentials (-4 and -4.5 V vs. Graphite) showed starkly contrasting dark borders surrounding the treated central area. It appears that reduction products weren't absorbed as easily into the felt tip as was the case for the highly absorbent sponge material. Therefore, polluting agents from the saturated felt tip may have been re-deposited onto the surface of the Ag coin. The circular motions performed with the pencil during treatments may have transported reaction products to the outskirts of the cleaned area.

Significant scratch marks in the sample surface were observed in spots treated with a felt tip at strongly negative potentials (Fig. 55 centre). This was not the case where the electrolytic treatment was carried out using a pad manufactured from the AION Clean Room Sponge. Figure 6 shows the border region between treated and untreated areas of the spot treated with a felt tip at a potential of -4.5 V vs. Graphite. It is apparent that the scratch marks stem from the circular motion of the electrolytic pencil during the treatment.

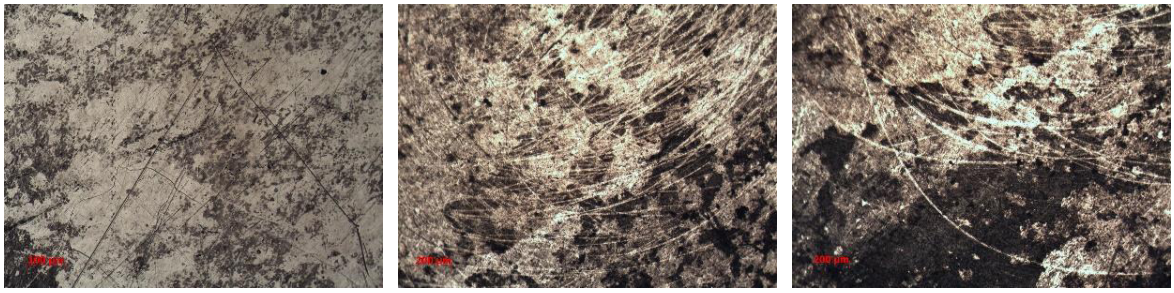


Fig. 55: Optical micrographs of surfaces treated at -4.5 V vs. Graphite for 60 seconds using pad made from AION Clean Room Sponge (left) and felt tip (centre) and border region of spot test carried out with felt tip (right)

5.5.7. Conclusion

The electrolytic treatment of historic artefacts made from silver and silver alloys with an electrolytic pencil is a method that has clear advantages over the more established techniques including chemical and mechanical tarnish removal. For one, it must be noted that at no point does the electrolytic treatment described in the present work require the use of hazardous chemicals. The electrolytic treatment carried out on a pair of naturally tarnished Ag sugar tongs was completed in less than an hour and the treated artefact only requires a soft polishing step as a follow-up in order to attain a more brilliant surface. To achieve the described result, several treatment steps were applied at increasing potential strengths and with the use of different contacting materials. This means that the cleaning parameters can be adapted to the surface to be cleaned. This, however, requires a certain level of experience in the handling of the pen and the selection of the appropriate current intensity.

A first overall treatment of metallic artefacts with the electrolytic pencil mounted with a sponge pad as contacting material can be followed by the targeted reduction of persistent tarnish marks with a felt tip in areas not accessible to a sponge pad. The felt tip is harder and can cause scratches on the surface of the treated artefact. Because of the hardness of the felt tip, there is a tendency to stronger mechanical pressure during the treatment, which is not the case with the sponge tip due to the material properties. In addition, it should be considered that the dense felt tip cannot absorb the used electrolyte as well as a soft sponge pad. This can lead to the renewed deposition of corrosion products on the cleaned surface. Careful use of the felt and frequent replacement of this cleaning agent with fresh and clean material is therefore recommended.

6. Long-term care and protection with possible conservation strategies

Consideration and development of preventive measures for the metal objects from the Theyer's collection, which can also be adopted for other similar collections and individual objects, are an essential aspect for their long-term preservation. This approach consists of indirect measures to slow down decay and prevent damage by creating optimal conditions for its preservation [167,168]. Preventive conservation stands for correct handling and use, transport, storage and presentation of cultural goods [169,170]. The analytical investigations carried out on this special collection from Technisches Museum Wien have created the basis for its further conservational considerations.

The condition of the objects was evaluated, the identification of the surface and bulk composition, possible residues of organic an anorganic coatings and the extent of possible changes, as well as the evaluation of the causes of the deterioration and the determination was investigadet. The remnants of silver, proven to be a conductive layer used in galvanic impression taking in Theyer's laboratory and transferred to varying degrees to the electrodeposited parts, form local elements that can accelerate local corrosion reactions. This also leads to increased roughness and thus to increased surface area and their reactivity with the surrounding air. Dirt layers and residues from the manufacturing process (e.g. electric ink or printing ink) also contribute to irregular tarnishing and corrosive changes of the surface. These surface properties affect long-term stability and the concrete applicability of such artifacts. Any corrosive changes of the printing surfaces are immediately reflected in the impression and affect the quality of the print.

After decades of storing the contents in a wooden cabinet, various types of damage have occurred. With the metal objects different corrosion phenomena could be observed from slight oxide formation up to stronger stain and corrosion formation. In addition to materials and processes, correct environmental conditions are important external factors that influence plate preservation. In order to prevent further changes, limited values for relative humidity and temperature were specified. Recommendations covering various aspects of storage conditions are listed in Table 16.

Table 16 Preventive storage and packaging conditions

Storage conditions	General storage material	May not adversely affect the objects
	Individual packaging	One plate per packaging unit to avoid friction Avoid contact with the frontside Always store flat Do not stack plates on top of each other / use sufficiently thick intermediate layers
Handling and monitoring	Handling	Handle plates by edges Allways wear gloves for handling
	Monitoring	Keep records of corrosion condition Keep records of any damage to the storage materials
Climate conditions	Temperature in the storage room	All-season: 18 °C +/- 2 °C
	Temperature in exhibition area	Preferably below 26 °C +/- 2 °C
	Humidity	Preferably below 40 % +/- 5 %
Airquality		Use filtered air or absorbent material

Gentle surface cleaning is recommended before long-term storage of the objects in the depot to remove the dirt deposits.

7. General conclusions and outlook

Within the scope of this work, the entire collection from the Theyer's Laboratory could be examined in detail and added to the museum's own database - including all results from scientific investigations, as well as the so-called fine indexing by the entry of all gained information about each individual object. Thus, the newly gained knowledge is available to all museum experts as well as to any interested person thanks to the online availability of the collection inventory database. This well researched collection in terms of cultural history and conservation science forms the basis for all further research work in the field of electrotyping and printing industry of the 19th century.

Within the scope of this work, some crucial insights into the activities of the first Austrian laboratory for electroplating technology have been gained. Many interesting details from their lives, their work, their unlimited motivation and the achievements of Franz Theyer and Erwin Waidele could be acquired. The level of knowledge about electrochemical deposition processes in the first period of application at the beginning of the 1840s was considerably increased. Galvanography, a technique that has remained relatively unknown until now, has been newly researched and the knowledge about its fingerprint characteristics has been gained and already partly published within the scope of this thesis. In addition, knowledge of the materials used, and their ageing properties was gained.

In the course of the work on the objects from the Theyers' laboratory, it became apparent that electroplating technology was closely related to early photography and its development in Vienna. Finally, both techniques were developed towards the end of the 1830s and immediately used and further developed with great enthusiasm. Often the same people - academics, merchants, craftsmen and artists - were testing and implementing these two techniques. Working groups such as the "Fürstenhofrunde" were quickly formed in Vienna, which enabled the participants to exchange ideas directly and thus to further develop their skills more quickly and easily. They used the knowledge and resources of each other and managed to take on one of the leading roles in Europe and worldwide with some inventions (e.g. development of the first mathematically calculated lens by Joseph Petzval, as well as a metal camera by the optician shop of the Voigtländer family in Vienna).

However, some inventions from this period remained unknown. Fundamental studies in the field of early photography by Joseph Berres, Erwin Waidele, Franz Kratochwila, Johann and Joseph Natterer are still unexplored and little known. A great find was made in the collection

of Franz Theyer and his companion Erwin Waidele. Under the printing plates one etched daguerreotype was discovered. This is the only preserved and probably the oldest photograph on a silver-plated copper plate prepared for duplication by printing. The presence of Cl in exposed areas confirms that Viennese photographers recognized, and applied advantages of other halides compared to I (presented and applied by Daguerre). The absence of Hg as a developer on the other hand testifies to the use of other photographic techniques than classical daguerreotype. The etching method of Joseph Berres, who most probably etched the above-mentioned plate, is described rudimentarily in the literature, but remained unknown in detail. The fact that such etched photographs on metal plates quickly lost their "profile" and were probably recycled or disposed of has meant that no such original plate has yet been found. Probably the preservation of the plate with the view of the Josef II's monument in Vienna can be attributed to the coincidence that it might have been sorted out after its production due to the visible defects in the marginal area. Certain aspects of the production process could be reconstructed and published based on historical written sources. The strong connection between photography and electroplating in the sense of duplication of printing plates in 1840s was also established.

A better understanding of reproduction habits and the disappearance of the boundary between original and copy in the second half of the 19th century was achieved. In fact, it is difficult to determine which print came from an original plate and which came from an electrodeposited copy of the original plates. The experimental series with three different conductive layers used historically and also today has brought more insight into the surface quality of galvanic copies of printing plates. These new observations will be invaluable in the identification and time allocation of graphic techniques in the future, as well as in the production of printing plates.

Based on the condition assessment and the damage analysis, a concept for conservation and storage could be developed. For this, the identification of very individual surface structures and remnants of the electro inks was of significant importance. The focus on this relatively small collection of electrotype objects allowed the research and development of a very broad base of fundamental facts for their better understanding, recognition and detection. Thus, the prerequisites for a well-founded museum presentation of this unusual collection were created.

Each plate can be seen as a work of art and undoubtedly deserves to be handeled individually and placed in the centre of attention.

Objects and above all the individual metal layers will continue to be researched in terms of material technology and technological history in order to better understand the details of different manufacturing processes. The study of the original written documents from the Theyer estate will as well be continued.

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Kunst-Nachrichten. Über Galvanoplastik und Galvanographie,
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Der Unterschied zwischen der Galvanoplastik und der Daguerreotypie als Kunstmittel besteht darin, daß der Erstere die Naturkräfte selbst das Geschäft des Künstlers, die Production, auf sich nehmen müssen, was sie zwar mit vieler Genauigkeit, aber nach starren, unbeugsamen Gesetzen thun, weil den Naturkräften, wie männiglich gekannt, innere Anschauung und lebendige Phantasie mangelt. Bei der Galvanoplastik sind die Naturkräfte dienende Mägde, sie formen das Gebilde welches der schöpferische Geist des Künstlers hervorrief, und welches daher ein inneres Leben in sich trägt, mit mikrometrischer Genauigkeit nach, sie schaffen nicht, sie sind nur Mittel der Vervielfältigung damit das Kunstwerk zu Geist und Herzen Vieler reden möge, und den Menschen aus der Alltäglichkeit hinüber zaubere, in das Reich des Schönen.

9. Supplementary Materials

Appendix I

Die Aufarbeitung von Originaldokumenten und anderen historischen Quellen aus dem Nachlass von Franz Theyer war ein wesentlicher Bestandteil dieser Arbeit, der die Grundlage für alle weiteren kulturtechnologischen Interpretationen bildete. Die Ergebnisse wurden in einer gemeinsamen Publikation mit dem zuständigen Kurator, Dr. Hubert Weitensfelder und Prof. Wolfgang Kautek im Auftrag des Technischen Museum Wien und des Österreichischen Forschungsinstituts für Technikgeschichte (ÖFIT) herausgegeben. Die Blätter für Technikgeschichte sind das österreichische Forum zur wissenschaftlichen Auseinandersetzung mit technikhistorischen Fragestellungen. Diese Publikation bietet einen breiten Überblick im technischen und historischen Kontext und wird als zusätzliche Informationsquelle dem Anhang beigelegt.

Die Anfänge der Galvanoplastik und Galvanografie in Österreich

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Herausgegeben im Auftrag des Technischen Museum Wien und des Österreichischen Forschungsinstituts für Technikgeschichte (ÖFIT). Die Blätter für Technikgeschichte sind das österreichische Forum zur wissenschaftlichen Auseinandersetzung mit technikhistorischen Fragestellungen.

Zusammenfassung

Das Technische Museum Wien (TMW) ist im Besitz einer großen Zahl von Gegenständen, deren Herkunft mitunter ausführliche Recherchen erfordert und bisweilen auch spannende Geschichten birgt. Eines der ungewöhnlichsten Objekte gelangte im Rahmen einer breit angelegten Inventur im Jahr 2009 in den Blickpunkt unserer Aufmerksamkeit. Es handelt sich um einen Kasten aus Eichenholz mit einer an der Oberseite angebrachten Beschriftung „Galvanoplastik und deren Anwendung. Franz Theyer, Wien 1839-1851“. Der Kasten enthielt in sieben Laden rund 20 Ausschnitte aus Zeitungen und Zeitschriften sowie Broschüren, über 50 Briefe, Verzeichnisse und andere handschriftliche Dokumente sowie Druckvorlagen aus Kupfer und Probeabdrucke. Die überlieferten Zeugnisse sind inzwischen Thema einer akademischen Arbeit. Auf den folgenden Seiten möchten wir in der gebotenen Kürze die Geschichte hinter diesen Objekten erzählen und einige Fragestellungen zu ihrer weiteren Erforschung formulieren.

Das „galvanoplastisch-artistische Laboratorium“ von Theyer und Waidele in Wien

Zunächst zum eingangs erwähnten Urhebers der Geschichte. Franz Seraphin Theyer (1809-1871) besaß in dritter Generation ein Geschäft für „Nürnberger Waren“, also Gegenstände für den Gebrauch bürgerlicher Haushalte. Dazu zählten auch Utensilien zum Schreiben und Zeichen, wie Farben, Leinwand, Öle und hochwertige Papiere. Die Handlung lag an der Ecke Kärntnerstraße-Weihburggasse, Nr. 905. Ihre zentrale Lage und die Art des Geschäfts ermöglichten Theyer leichten Kontakt zu künstlerisch-akademischen und anderen geistig aktiven Kreisen. Er selbst befasste sich bereits sehr früh mit der Daguerreotypie.[2] 1836 erhielt er ein Privileg (Patent) auf die Erfindung eines Bindemittels für alle Gattungen von Papiersiegeln auf einen Zeitraum von zwei Jahren.[3]

1839 wurde in Wien ein Niederösterreichischer Gewerbeverein gegründet. Im repressiven politischen Klima dieser Zeit erhielten nur wenige Vereine die behördliche Genehmigung. Dort organisierten sich Fabrikbesitzer, Gewerbetreibende und naturwissenschaftlich interessierte „Dilettanten“ im besten Sinne; sie befassten sich mit aktuellen Erfindungen und suchten nach Möglichkeiten, diese kommerziell umzusetzen. Dazu zählten u.a. die Daguerreotypie sowie eine Reihe von Verfahren, um mit Hilfe von Batterien die chemischen Auswirkungen des elektrischen Stroms technisch zu nutzen. Mehrere Unternehmer in Westeuropa beschichteten nunmehr Gegenstände auf elektrochemischem Weg mit Edelmetallen und lösten damit traditionelle Prozesse wie die Feuervergoldung und die Silberplattierung hinter sich. Dazu zählte die Firma Elkington und Mason in Birmingham sowie der Goldschmied Charles Christofle in Paris.

Diese Beschichtungstechniken mit dem Ziel einer dauerhaften Verbindung zweier Metalle wurden von den Zeitgenossen als „Galvanostegie“ bezeichnet. Auf denselben elektrochemischen Grundlagen basierte die „Galvanoplastik“, die aber einem anderen Zweck diente: Hier

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[2] Vgl. Theodor Theyer: Die Industrie der Papier-Ausstattung in Österreich. Wien 1908, S. 45, und Rudolf Granichstädten-Cerva, Julius Mentschl, Gustav Otruba: Altösterreichische Unternehmer. Wien 1969, S. 121 f.

[3] K.k. allgemeine Hofkammer (Hg.): Beschreibung der Erfindungen und Verbesserungen, für welche in den kaiserlich-königlichen österreichischen Staaten Patente ertheilt wurden, und deren Privilegiums-Dauer nun erloschen ist. 6 Bände. Wien 1841-1847. Band 2 (1842), S. 32.

wurde die Oberfläche eines Gegenstandes mit Kupfer beschichtet, anschließend wurde die so erzeugte Platte aber entfernt und bildete nun in bislang ungekannter Feinheit einen Negativabdruck des Originals. Als Erfinder dieses Verfahrens gilt der deutsche Physiker Moritz Hermann von Jacobi, der in St. Petersburg forschte und 1840 in einer Broschüre mit dem Titel „Die Galvanoplastik“ über seine Versuche berichtete. Eine frühe praktische Anwendung dieser Technik entwickelte der in München lebende Mineraloge und Schriftsteller Franz von Kobell. Er nutzte sie, um in Tuschmanier gemalte Bilder und Zeichnungen auf galvanischem Weg in Kupferplatten vertieft zu kopieren. Von diesen konnten wiederum Negative genommen werden, die in der Folge eine theoretisch beliebige Anzahl von Abdrücken der Kunstwerke ermöglichten, ohne dass die Qualität der Originalplatten darunter litt. Kobell machte sein Verfahren ebenfalls 1840 öffentlich und nannte es „Galvanographie“.

Bereits diese wenigen Namen signalisieren, dass Forschungen zur Galvanotechnik in einem europäischen Kontext stattfanden. Im Niederösterreichischen Gewerbeverein stießen sie auf großes Interesse, wie aus einer Reihe von Beiträgen in dessen Zeitschrift deutlich wird. Bereits in einer Monatsversammlung vom 3. August 1840 stellte der Wiener Tapetenfabrikant Michael Spoerlin einen Antrag, in den Räumlichkeiten des Vereins einen galvanischen Apparat aufzustellen, um Experimente mit dieser neuen Technik zu ermöglichen.[4] Franz Theyer trat dem Gewerbeverein offenbar zwischen Oktober und Dezember 1841 bei.[5] Damals befasste er sich bereits mit Versuchen zur Anwendung der Galvanoplastik und berichtete darüber in der Monatsversammlung am 4. Juli 1842. Seine Anliegen waren die Erzeugung hochwertiger glatter Platten für Kupferstecher auf elektrolytischem Weg, die Herstellung von Kopien gestochener Platten sowie die Galvanografie im engeren Sinn. Für sein erstes Ziel nannte er positive Rückmeldungen bekannter Kupferstecher, die sich bislang über poröse Stellen und Aschenflecken auf den traditionell erzeugten Platten geärgert hatten. Zum Zweck der

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[4] Michael Spoerlin: Industrielle Mittheilungen und Antrag zur Aufstellung eines galvanoplastischen Apparates, in: Verhandlungen des niederösterreichischen Gewerb-Vereins 1 (1840), S. 105-107. Ferner: Andreas Baumgartner: Über Metallfällungen durch Elektricität im Allgemeinen und über Galvanoplastik insbesondere, in: ebd., 2 (1841), S. 122-131; Franz Freiherr von Leithner: Bericht der Abtheilung für Chemie und Physik über die Aufstellung galvanoplastischer Apparate im Vereins-Lokale, in: ebd., 132-135; Andreas Baumgartner, Nachtrag zur Galvanoplastik, in: ebd., 3 (1841), S. 66-68; Ders.: Bericht des Sekretärs der Abtheilung für Chemie, in: ebd., 4 (1841), S. 162-169, hier S. 166 f.

[5] Stand des niederösterr. Gewerb-Vereins am Ende des Jahres 1841, in: Verhandlungen des niederösterreichischen Gewerb-Vereins 6 (1842), S. 59-97, hier S. 89.

Vervielfältigung experimentierte Theyer mit allen Arten von Kupferstichen, auch mit geschabten, Trockennadel- und Aquatintaplatten. Damit sei er nun imstande, „eine beliebige Anzahl strengster Doubletten einer Original-Kupferplatte zu erzeugen, was die Anfertigung von Kunstvereinsblättern, Diplomen, Landkarten, und überhaupt bei allen jenen Kunstblättern Berücksichtigung verdient, von welchen eine große Anzahl von Abdrücken erfordert wird, und zu welchem Zwecke bis jetzt Stahl verwendet wurde.“ Bei der Galvanografie ging es ihm darum, „auf eine glatte Metallplatte in Tuschmanier mit Firnißfarbe zu malen; da die Schatten immer pastioser aufgetragen werden, so bildet das Gemälde ein Reliefbild, und die darüber gebildete galvanische Platte ist alsogleich für den Druck anwendbar.“[6]

Für seine Versuche tat sich Theyer mit Erwin Waidele zusammen. Über diesen ist nicht viel bekannt. 1839 hatte Waidele zusammen mit einem Wiener Spengler ein „Lunar-Licht“ patentieren lassen; dabei wurde für andere Zwecke ungeeignetes Öl, Teeröl oder ein Öl-Harzgemisch zur Beleuchtung verwendet. In diesem Privileg, das nach zweijähriger Dauer erlosch, wurde Waidele als Hörer des dritten Jahrgangs im Medizinstudium bezeichnet.[7] Er beendete dieses und wurde in späteren Berichten als Doktor der Medizin bezeichnet. Waidele beschäftigte sich ebenso wie Theyer intensiv mit der Daguerreotypie.[8]

1842 erschien ein erster größerer, zweiteiliger Bericht über die Bemühungen Theyers und Waideles. Sein Verfasser richtete zunächst einen historisierenden Blick auf die Kunst der Kupferstecher. Ihre Leistungen hätten es ermöglicht, Stiche von Gemälden mittels Vervielfältigung durch den Druck einer größeren Zahl von Interessenten zugänglich zu machen, welche sich keine Originale leisten konnten.

Damit habe der Kupferstich für Geschmackbildung und Kunstkenntnis fast ebenso viel geleistet wie der Buchdruck für die Verbreitung von Wissen. Da die in weiches Kupfer gesto-

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[6] Ebd., 8 (1843) S. 53-56; die Zitate S. 55, 56.
[7] Hofkammer (Hg.), siehe Anmerkung 2, Band 2, S. 151 f.
[8] Anton Martin: Handbuch der Photographie oder vollständige Anleitung zur Erzeugung von Lichtbildern auf Metall, Papier und auf Glas, Daguerreotypie, Talbotypie, Niepçotypie. 2. umgearbete und vermehrte Auflage Wien 1851, S. 46, 91, 145; Maren Gröning: Inkunabeln einer neuen Zeit. Pioniere der Daguerreotypie in Österreich, in: Dies., Monika Faber: Inkunabeln einer neuen Zeit. Wien 2006 (= Beiträge zur Geschichte der Fotografie in Österreich 4), S. 8-47, hier S. 21 f.

chenen Platten, so der Autor weiter, nur eine begrenzte Zahl von Abdrücken für ein wachsendes Publikum lieferten, habe sich der Stahlstich verbreitet, der eine rund zehn Mal höhere Auflage erlaubte. Doch habe dessen härtere Oberfläche den Künstlern große Probleme bereitet. Dieses Dilemma werde nun durch die Galvanoplastik beseitigt. Mit ihrer Hilfe ließen sich vom Original eines Kupferstichs beliebig viele und höchst präzise Matritzen erstellen, die wiederum eine praktisch unendliche Menge von Abzügen ermöglichten.

Der Autor stellte auch weitergehende ökonomische Betrachtungen an. In Zukunft würden nun nicht mehr Kunstspekulanten Stahlstiche nach Kupferstichen anfertigen lassen, sondern die Verleger müssten vielmehr den Kupferstechern das Recht abgelten, galvanoplastische Nachbildungen vom Original nehmen zu lassen. Bachmann bezeichnete die neue Technik als „Milchschwester“ der Daguerreotypie, die in Wien ebenfalls frühe Aufnahme gefunden und eine rasche Entwicklung genommen hatte.[9] Als weiteren Vorteil führte er an, dass das galvanisch erzeugte Kupfer bei hoher Reinheit eine gleichförmige Struktur aufwies und damit das handelsübliche Metall bei weitem übertraf. Diese Eigenschaften ermöglichten reine Schnitte oder Linien auf einer besonders planen Oberfläche. Daher arbeiteten bereits mehrere Wiener Kupferstecher ausschließlich mit einem solcherart gewonnenen Kupfer. Um die Qualität der Erzeugnisse zu belegen, wurden im „Journal“ der Abdruck einer vom Wiener Kupferstecher Johann Nepomuk Passini verfertigten Platte einem weiteren, von einer galvanischen Platte des Originals stammenden gegenübergestellt. Vom Original, so Bachmann, waren bereits 3600 Abdrücke gewonnen und einem Taschenbuch beigelegt worden, dazu kamen jene für die Auflage des „Journals“. In Zukunft würden breitere gebildete Schichten in die Lage versetzt, erstklassige Abdrücke zu erwerben. Dennoch stehe nicht zu befürchten, dass Kunstwerke durch eine größere Verbreitung an Wert verlieren würden.[10]

Theyer und Waidele nutzten bald eine weitere Gelegenheit, ihr Verfahren für Kunstwerke in größerer Auflage zu erproben, indem sie die Gestaltung der Wiener Neujahrsglückwunsch-Enthebungskarten für 1843 besorgten. Solche Karten wurden von begüterten Bürgern erworben, der Erlös kam den Armen zugute. Die Namen der Käufer bzw. Wohltäter wurden in

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[9] Dr. Julius Bachmann: Über die galvanoplastisch-artistischen Leistungen von Theyer und Waidele in Wien, in: Allgemeines Wiener Polytechnisches Journal, 20.8.1842, S. 409 f.
[10] Ebd., 23.8.1842, S. 415 f.

einer Liste veröffentlicht, für sie entfiel damit die Notwendigkeit, ihren Bekannten bzw. Kunde persönlich Neujahrswünsche zu übermitteln. Zur Herstellung von Karten für 1843 stellten der Kupferstecher Josef Stöber die Kupferplatten für ein größeres und die Buchhändlerswitwe Philippine Haas jene für ein kleineres Blatt unentgeltlich zur Verfügung. Als Vorlage für das größere Blatt diente das Gemälde „Der Blumenaltar" des Holländers Jan Davidsz de Heem, während der Kupferstecher Josef Axmann ein kleineres Votivbild nach Paolo Veronese lieferte. Theyer erzeugte auf seine Kosten für die größeren Blätter 16, für die kleineren sechs Kupferplatten und finanzierte außerdem deren Drucklegung in vier Werkstätten. Die Glückwunsch-Enthebungskarten lagen beim Stadtmagistrat, in den Wiener Pfarrämtern sowie in dem Räumlichkeiten der „Wiener Zeitung" zum Erwerb auf. Bis Mitte Jänner 1843 kam die stattliche Summe von 8256 Gulden und 22 Kreuzern Kurantwährung zusammen. Davon wurden 1000 Gulden für mittellose entlassene Sträflinge des k.k. Niederösterreichischen Provinzial-Strafhauses bestimmt, einen weiteren Betrag verteilten die Wiener Pfarren an bedürftige Personen.[11] Der Wiener Bürgermeister Ignaz Czapka bedankte sich bei Theyer für dessen Engagement, der Magistrat ließ ihm die goldene Salvator-Medaille zukommen.[12]

Zur Qualität der Motive für die Wiener Enthebungskarten äußerte sich in der Monatsversammlung des Gewerbevereins vom 6. Februar Johann Trost, ein Professor an der Akademie der bildenden Künste. Er berechnete, dass für 18.000 Abdrücke galvanischer Kupferplatten von de Heems großformatigem „Blumenaltar" die Kosten pro Blatt sich lediglich auf zwei bis drei Kreuzer Kurantwährung beliefen. Auch Kenner seien nicht imstande, Abdrücke der Original-Kupferplatte von jenen der galvanoplastischen zu unterscheiden. Theyer und Waidele erhielten die kleine goldene Medaille des Gewerbevereins zugesprochen.[13]
Bald darauf interessierte sich auch die staatliche Warenstempel-Prüfungskommission für die neue Technik. Den Anlass dazu gab die Befürchtung, diese könnte die Fälschung von Stempeln erleichtern, welche die inländische Herkunft einer Ware zertifizierten. Deshalb bat man

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[11] Wiener Zeitung, 16.1.1843, S. 117.
[12] TMW Archiv: Schreiben an Theyer; Wien, 19.1.1843.
[13] Johann Trost: Bericht der Abteilung für Physik über die Leistungen der Herren Theyer und Waidele im Gebiete der Galvanoplastik und Galvanographie, in: Verhandlungen des niederösterreichischen Gewerb-Vereins 9 (1843), S. 56-59.

Theyer, darüber vor einer Kommission von Beamten und Sachverständigen genauer zu berichten.[14]

Noch im gleichen Jahr, 1843, machten Theyer und Waidele ihre Erzeugnisse einem größeren Publikum bekannt. Anlässlich der 21. Versammlung des renommierten Vereins deutscher Naturforscher und Ärzte in Graz zeigten sie eine Auswahl ihrer Produkte, dazu erschien eine kleine Broschüre. Ferner wurde eine galvanografische Platte ausgestellt, die von Erzherzog Stefan gefertigt worden und mit seinem Namenszug versehen war. Darüber hinaus ließ das Labor nun Kirchengeräte des Bronzearbeiters Josef Fleisch in Wien vergolden und versilbern, die von Martin Theyer und seinem Sohn Franz in Wien vertrieben wurden.[15] Zitate und Paraphrasen aus dieser Broschüre erschienen auch im Grazer „Innerösterreichischen Industrie- und Gewerbe-Blatt", welches von Karl von Frankenstein herausgegeben wurde.[16] Dieser zählte selbst zu den frühesten Anwendern der Galvanotechnik in Österreich. Er erhielt 1843 ein Privileg auf ein Verfahren, um Gegenstände ohne Verwendung einer Batterie galvanisch zu vergolden und zu versilbern.[17]

Nach der Ausstellung in Graz stellten Theyer und Waidele die dort gezeigten Exponate im November 1843 auch im Gebäude des Wiener Kunst-Vereins im Volksgarten aus. Der Besuch war kostenlos, aber „zur Bequemlichkeit, und um den allgemeinen Zudrang abzuhalten" konnten Interessenten die Eintrittskarten dafür in Theyers Handlung abholen.[18] Im ersten Saal präsentierten sie acht Kopien gestochener Kupferplatten, galvanisch erzeugte Platten für Kupferstecher und galvanische Vergoldungen von Kirchenornamenten und Militärrüstungen sowie ihr Arbeitsgerät, eine galvanische Batterie. Im zweiten Saal konnten die Besucher die Abdrücke herkömmlicher und galvanischer Platten unmittelbar miteinander vergleichen und sich so ihr eigenes Urteil bilden.[19]

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[14] TMW Archiv: Schreiben an Theyer; Wien, 2.5.1843. Dazu ein Dankschreiben; Wien, 12.1.1844.
[15] Verzeichniss der bei Gelegenheit der 21sten Versammlung deutscher Naturforscher und Ärzte in Grätz aufgestellten Producte der Galvanoplastik und Galvanographie aus Franz Theyer's erstem galvanoplastischem Laboratorium in Wien No. 905. Wien 1843, S. 4 f.
[16] Allgemeines Anzeige-Blatt für technische Literatur, Industrie, Handel, Künste und Gewerbe. Beilage zum Innerösterreichischen Industrie- und Gewerbe-Blatt, 27.9.1843.
[17] Hofkammer (Hg.), siehe Anmerkung 2, Band 5 (1847), S. 50 f.
[18] Wiener Zeitung, 14.11.1843, S. 2347.
[19] W-r: Ausstellung galvanoplastischer Producte aus dem galvanographischen Institute des Franz Theyer, in: Der Wanderer im Gebiete der Kunst und Wissenschaft, Industrie und Gewerbe, Theater

Die Schau im Volksgarten nahm ein anderer Kunstfachmann zum Anlass, die Auswirkungen der neuen Technik auf das künstlerische Schaffen unter die Lupe zu nehmen. Nach seinen Ausführungen waren die Künstler bislang auf zwei Techniken beschränkt, wenn sie ihr Werk selbst vervielfältigen wollten, nämlich auf die Radierung und die Lithografie. Erstere erforderte viel Erfahrung im Umgang mit Radiernadel und Ätzmitteln. Die Lithografie wiederum gewährleistete auf den ersten Blick ein leichteres, zeitsparendes Werken auf größeren Flächen; doch war auch hier ein fachmännischer Umgang mit der chemischen Kreide vonnöten. Die Galvanografie ermöglichte es dem Künstler hingegen, mit einer braunen Firnisfarbe das gewünschte Motiv auf eine matt versilberte Kupferplatte zu malen. Über dem so erzeugten Reliefbild wurde dann galvanisch eine zweite Platte hergestellt, die ebenso viele Abdrücke wie eine geschabte oder radierte Platte und darüber hinaus überhaupt die Herstellung beliebig vieler Druckplatten gestattete. Somit konnten die Künstler dieselbe Technik anwenden wie bei der Ölmalerei, mit dem Unterschied, dass sie nur mehr mit einer Farbe arbeiteten, die Präzision des galvanischen Prozesses machte die Ätzung fast überflüssig. Der Autor sprach der Galvanografie für die Darstellung von Landschaften, Gebäuden und Tieren große Bedeutung zu; eine Anwendung für die Vervielfältigung größerer Genre- und historischer Darstellungen lasse sich aber noch nicht sicher vorhersagen.[20]

In einem weiteren Beitrag thematisierte der gleiche Verfasser Bedenken von Künstlern gegen die Galvanografie. So befürchteten manche, dass ihre Originalwerke durch eine galvanografische Vervielfältigung an Wert verlieren würden. Doch würden diese auch in Zukunft vom gleichen Personenkreis erworben werden, der sich schon bisher den Erwerb von Originalen habe leisten können. Auf den Einwand einer geschäftsschädigenden „Kunstsättigung“ wurde entgegnet, die neue Technik würde lediglich minderwertige Vervielfältigungen vom Markt verdrängen, insgesamt aber das Niveau künstlerischer Reproduktionen anheben.[21]

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und Geselligkeit, 22.11.1843, S. 1111. Notizen zu dieser Ausstellung auch in: Der Sammler. Ein Unterhaltungsblatt für alle Stände, 16.11.1843, S. 739, und in: Wiener Zeitschrift für Kunst, Literatur, Theater und Mode, 16.11.1843, S. 1823 f. Anlässlich der Ausstellung versuchte ein weiterer Verfasser, den Leserinnen des Blattes in einer, wie er meinte, leichtverständlichen und humorvollen Art, das Thema „Galvanoplastik“ zu schildern: T. S.: Galvanoplastisches und Weibliches. Zerstreute Gedanken, in: Der Humorist, 23.11.1843, S. 939 f.

[20] Dr. E. Melly: Die Galvanografie in ihrem Verhältnisse zur Kunst. Aus Anlaß der Ausstellung im Volksgarten, in: Sonntags-Blätter, 19.11.1843, S. 1119-1122.

[21] Dr. E. Melly: Künstlerbedenken gegen Galvanografie, in: Kunstblatt. Beilage zu den Sonntagsblättern, 3.12.1843, S. 1173-1176.

Auch ein weiterer Autor knüpfte an die Ausstellung im Volksgarten Überlegungen zu verschiedenen Verfahren an. Die Galvanografie erlaube den Malern, ihre Werke mit den gewohnten Utensilien zu verfertigen und sie dann ohne Mittelsmann selbst der Vervielfältigung zuzuführen. Der Kupferstich vermittle mehr Wärme und Kraft als Lithografie und Stahlstich; und mit Hilfe der Galvanografie könnten diese Qualitäten nun in einer beliebigen Zahl von Abdrücken zum Ausdruck gebracht werden. Der Verfasser verglich die Galvanografie auch mit der Daguerreotypie. Er schrieb: „Der Unterschied zwischen der Daguerreotypie und der Galvanoplastik als Kunstmittel besteht darin, daß bey ersterer die Naturkräfte selbst das Geschäft des Künstlers, die Production, auf sich nehmen müssen, was sie zwar mit vieler Genauigkeit, aber nach starren, unbeugsamen Gesetzen thun, weil den Naturkräften, wie männiglich bekannt, innere Anschauung und lebendige Phantasie mangelt. Bey der Galvanoplastik sind die Naturkräfte dienende Mägde, sie formen das Gebilde, welches der schöpferische Geist des Künstlers hervorrief, und welches daher ein inneres Leben in sich trägt, mit mikrometrischer Genauigkeit nach, sie schaffen nicht, sie sind nur Mittel der Vervielfältigung, damit das Kunstwerk zu Geist und Herzen Vieler reden möge, und den Menschen aus der Alltäglichkeit hinüber zaubere in das Reich des Schönen.“[22]

Nach den Ausstellungen in Graz und Wien richtete Theyer im Dezember 1843 ein Majestätsgesuch an Kaiser Ferdinand. Zunächst schilderte er die Vorteile seines Verfahrens: Die Künstler könnten nun zur Erzielung großer Auflagen ihrer Werke auf den kostspieligen und mühsamen Stahlstich verzichten. Die galvanoplastischen Kopien der Kupferstiche ermöglichten durch die höhere Auflagenzahl dieselben Preise wie dieser. Darüber hinaus lieferte die Methode hochwertige Kupferplatten. Als zukünftige Einsatzgebiete für seine Technik nannte Theyer geografische Karten, Werke mit höheren Auflagen (z.B. erklärende Tafeln für Schulbücher), kalligrafische Vorschriften für Schulkinder, amtliche Dokumente und Staatspapiere, militärische Reglements und Ordensstatuten mit beigelegten Tafeln sowie Diplome. Darüber hinaus sollte die Galvanoplastik zur Verbreitung guter und geschmackvoller Bilder religiösen Inhalts beitragen und den Künstlern neue Erwerbsmöglichkeiten eröffnen. Theyer verwies in seinem Gesuch auf die erheblichen Ausgaben, die er bereits getätigt hatte, und bat

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[22] Wiener Zeitung, 18.12.1843, S. 2641 f; das Zitat S. 2641.

um eine jährliche Unterstützung in der Höhe von 1000 Gulden. Für den Fall, dass die Staatsverwaltung sein Verfahren übernehmen wolle, bot er an, dieses zu einem guten Preis abzutreten.[23]

In den folgenden Monaten verzichtete Theyer auf größere Auftritte in der Öffentlichkeit, doch wurde weiterhin fleißig gearbeitet. Allein 1844 erzeugte er 374 galvanisierte Platten. Darunter waren ein Stich von Johann Passini nach dem Gemälde „Die beiden Foscari“ des Malers Francesco Hayez für eine Gabe des Wiener Kunstvereins an seine Mitglieder und eine Radierung von Karl Rahl nach dem Bild „Hiob“ von Georg Friedrich Wächter für den Stuttgarter Kunstverein. Weitere Platten und Abzüge gingen an den Innsbrucker Kunsthändler Franz Unterberger, sie enthielten Abbildungen der Bronzestatuen in der dortigen Hofkirche. Neben dem Standort in der Innenstadt wurde auch der Wiener Vorort Unter St. Veit Nr. 36 als neue Adresse genannt.[24]

Erwin Waidele erhielt Ende 1843 oder Anfang 1844 die Stelle eines Adjunkten am chemischen Laboratorium des Polytechnischen Instituts in Wien.[25] Nach einem Aufenthalt beim berühmten Chemiker Justus Liebig in Gießen reiste er im September 1844 nach Paris, um sich hier über den Stand der Galvanotechnik und insbesondere der Galvanografie zu informieren. In einem Brief an Theyer, den er als lieben teuren Freund bezeichnete, berichtete er über seine Beobachtungen. So hatte er sich über die „galvanisation du fer“ kundig gemacht, bei der es sich um Verzinkungen von Eisen zum Zweck des Korrosionsschutzes handelte. In den Läden hatte er viele Büchsen mit verziertem weißem Metallüberzug gesehen, der ihn an versilbertes oder verzinntes Kupfer erinnerte. Er empfahl die Herstellung verzierter dünner Metallbleche; diese könnten von Buchbindern als Metallpapier benützt bzw. in etwas stärkerer Ausführung von Plattierern, Spenglern oder Bronzefabrikanten verarbeitet werden.[26] In einem weiteren Schreiben vom März 1845 erwähnte Waidele den Kupferstecher Friedrich

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[23] TMW Archiv: Theyer an den Kaiser; Wien, 10.12.1843.
[24] TMW Archiv: Schreiben Theyer; Wien, 27.6.1845.
[25] Monika Faber: „… ein gutmüthiger Privat-Thor“. Die Fotografie am Chemischen Laboratorium des Polytechnicum in Wien, in: Fotogeschichte 22/83 (2002), S. 21-37, hier S. 26.
[26] TMW Archiv: Waidele an Theyer; Paris, 19. und 25.10.1844.

von Martens, der in Paris für Theyer Platten bearbeitete.[27] Martens befasste sich darüber hinaus engagiert mit der Daguerreotypie und bat Theyer seinerseits mehrfach um die Übersendung eines Kamera-Objektivs, das dieser ihm versprochen hatte.[28] Martens berichtete ferner, dass ihm Theyers Platten viel Mühe bereiteten. Schließlich übersandte er ihm aber zwei fertiggestellte Platten, als Motive nannte er das in Salzburg gelegene Wiesbachhorn (Abb. 1) und eine Straßenszene in Prag.[29] Erneut bat er Theyer um die Zusendung eines Objektivs, und zwar aus der Werkstatt des renommierten Wiener Optikers Peter Wilhelm Friedrich von Voigtländer.[30]

Seit Oktober 1844 befasste sich Theyer mit einer weiteren Verbesserung der Galvanografie. Die versilberten Platten, auf denen die Künstler ihre Zeichnungen auftrugen, irritierten manche von ihnen. Ihre Öl-, Firnis- und Harzfarben ließen sich außerdem oft nur mit Mühe auftragen und trockneten bisweilen erst nach drei Monaten. Darüber hinaus konnten die Künstler keine reinen Tuschtinten verwenden, die sie von Zeichnungen in Aquarell- oder Tuschmanier gewohnt waren. Solche Einschränkungen verminderten aber die Qualität ihrer Werke. Theyer entwickelte daher in der Folge eine neuartige Substanz, die er als „Elektrotinte“, bezeichnete.[31] Ihre Wirkung wurde folgendermaßen charakterisiert: „Es wird dem Künstler möglich gemacht, durch bloßes Zeichnen mit der Feder oder der Kreide, durch Laviren mit dem [!] Tusche, oder auch durch Vereinigung dieser gewohnten und geübten Methoden, sein Geistesprodukt sogleich zur unbeschränkten Vervielfältigung tauglich und so zur größtmöglichen Publizität gebracht zu sehen. Diese Erfindung ist Elektrotinte genannt. Die chemischen Tusche [!] und Kreide sind eigens dazu bereitet, und das Papier gleichfalls hiezu präparirt. Es ist dem Künstler nichts mehr hinderlich, selbst alle feinen Handgriffe der englischen Aquarellmalerei, durch Herausheben von Tönen oder Auskratzen der Lichter mit Schabmessern oder Nadelspitzen können angewendet werden. Die so erzeugte Zeichnung wird der galvani-

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[27] TMW Archiv: Waidele an Theyer; Paris, 6.3.1845.
[28] TMW Archiv: Martens an Theyer; Paris, 22.11.1844; 3.1.1845.
[29] TMW Archiv: Martens an Theyer; Paris, 6.3.1845; 15.3.1845.
[30] TMW Archiv: Martens an Theyer; Paris, 20.4.1845.
[31] Carl Roesner; Bericht über die Electrotinte des Herrn Franz Theyer. (Vorgetragen in der Monatsversammlung am 2. Juni 1845), in: Verhandlungen des niederösterreichischen Gewerb-Vereins 13 (1847), S. 8-11. Roesner war Professor an der Akademie der bildenden Künste.

schen Kopiatur übertragen, und binnen höchstens acht oder zehn Tagen (nach der verschiedenen Dimension) erscheint die Zeichnung auf Kupfer, und liefert Abdrücke, der Originalzeichnung vollkommen gleich.“ [32]

Abb.1 Das Wiesbachhorn, Österreich, um 1845, BPA-015564-7 (163c).
Quelle: Archiv Technisches Museum Wien

Seine Neuerung präsentierte Theyer erneut bei einer Gelegenheit, die ihm breite Öffentlichkeit verschaffte, nämlich auf einer großen Gewerbeausstellung, die 1845 in Wien über die

[32] L. Rdtz.: Die Leistungen des Herrn Franz Theyer in Wien im Fache der Galvanographie und seine neueste wichtige Erfindung, in: Wiener Bazar. Wöchentliches Beiblatt zur Zeitschrift „Der Humorist“, 24.5.1845, S. 85 f, das Zitat S. 85.

Bühne ging.[33] Insgesamt zeigte Theyer dort 122 Objekte.[34] Im Zusammenhang mit der Vorbereitung und Durchführung dieser Ausstellung sind einige weitere Korrespondenzen überliefert. So übermittelte ihm Major Ferdinand Freiherr von Augustin in St. Pölten einen Zeichenversuch mit der „chemischen Tusche", wobei er klagte, es sei nicht angenehm, mit diesem Mittel zu arbeiten.[35] Ferner korrespondierte Theyer mit Louise Baronin Kotz. Aus einem ihrer Schreiben an ihn geht hervor, dass er Bilder für Marienwallfahrten produzieren wollte; anlässlich der weit verbreiteten Wallfahrtskultur bot sich hier ein großer Absatzmarkt.[36] In einem weiteren Brief bat die Baronin zum Zusendung von Abdrücken volkstümlicher Motive, nämlich eines Zipserhauses aus den Karpaten und eines türkischen Brunnens. Sie vermutete, Theyer werde auch in Prag viele Abnehmer für seine Erzeugnisse finden.[37] Im mährischen Frain / Vranov nad Dyyí stand Theyer mit einer Steingut- und Wedgwood-Manufaktur in geschäftlichem Kontakt. Dort wurden Motive von Kupferstichen auf das von ihr erzeugte Geschirr übertragen, die Firma übersandte Platten zur Galvanisierung.[38] Nach Triest schickte Theyer Abdrücke für ein Blatt des dortigen Kunstvereins. Ein Graf Waldheim ersuchte ihn um weitere Vorschläge, die den Zielen des Vereins entsprachen.[39]

Somit gelang es Theyer und Waidele, die Erzeugnisse ihres Betriebs nicht nur in Wien, sondern auch in anderen Kronländern bekannt zu machen. Darüber hinaus kamen aber auch Kontakte in mehrere deutsche Staaten sowie nach Frankreich und Russland zustande. In Berlin gelang dies bereits 1843. Dort wurde am 6. April der Grundstein zu einem königlichen

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[33] Verzeichniss der im Jahre 1845 in Wien öffentlich ausgestellten Gewerbs-Erzeugnisse der österreichischen Monarchie nebst den Namen der Aussteller in chronologischer Ordnung der Statt gefundenen Einsendungen. Wien 1845, S. 188. Erwähnt werden „Kupferplatten auf galvanischem Wege erzeugt und Abdrücke von solchen".
[34] TMW Archiv: Schreiben Theyer; Wien, 27.6.1845.
[35] TMW Archiv: Augustin an Theyer; St. Pölten, 18.7.1845. Augustin, ein Sohn des Vinzenz Freiherrn von Augustin, machte sich neben seiner militärischen Laufbahn u.a. durch Reiseberichte über Marokko, Spanien und die Alpen sowie durch Romane einen Namen: vgl. Helmut Neuhold: Der Raketenmacher. Vinzenz Freiherr von Augustin und der technische Fortschritt in der k.k. Armee. Diplomarbeit masch. Wien 1998, S. 161-163.
[36] TMW Archiv: Louise Baronin Kotz an Theyer; Heiligenkreuz (bei Bischofteinitz / Horšovský Týn in Westböhmen), 19.11.1844.
[37] TMW Archiv: Louise Baronin Kotz an Theyer; Prag, 25.8.1845.
[38] TMW Archiv: Josef Doré an Theyer; Frain, 19.11.1844; 4.7.1845; 3.9.1845.
[39] TMW Archiv: Graf Waldheim an Theyer; Triest, 1.2.1845.

Museum gelegt. Bei dieser Gelegenheit begutachteten der Monarch mit seiner Familie, Angehörige des Hofstaats, Mitglieder der Akademie der Wissenschaften sowie Professoren der Universität in der Gemäldegalerie galvanoplastische Erzeugnisse Theyers und Waideles. Angeblich betrachtete man diese „als das gelungenste und großartigste, was in diesem Fache bisher geleistet wurde.“ Der berühmte Naturforscher Alexander von Humboldt sprach ihnen mehr Qualität zu als allem, was er dazu in Paris gesehen habe.[40] Der preußische König verlieh Theyer und Waidele dafür eine goldene Kunstmedaille.[41] Ende 1843 schrieb aus Halle an der Saale Albert Klotz, Lehrer für Gehörlose und Vorsteher der Taubstummenanstalt, einen Dankesbrief für den Erhalt galvanisierter Druckplatten.[42]

1844 gab das Wiener „Kunstblatt“ Bemerkungen Franz von Kobells, des Erfinders der Galvanografie, wieder, die dessen Berichten an die Bayerische Akademie der Wissenschaften entstammten. Kobell datierte seine erste galvanografische Platte auf das Jahr 1840, sie war als Probe zu seiner Abhandlung zu diesem Thema in „Erdmanns Journal“ erschienen. An hervorragenden Erzeugern galvanografischer Erzeugnisse nannte Kobell in München Leo Schöninger und Josef Anton Freymann, in Wien Theyer und Waidele, zu deren Produkten er meinte: „Sie sind fast alle nur durch Malen der Bilder in Tuschmanier gefertigt, wie man solches aus den Abdrücken ersehen kann. Gewiß ist, daß diese Art die originellste Seite der Galvanographie ausmacht und für Landschaften, Baumgruppen, Thiere, Blumen etc. besonders vortheilhaft auszuführen ist.“[43]

Aus Leipzig wandte sich außerdem der Buchhändler und Verleger Heinrich Brockhaus an Theyer und ersuchte um Informationen, unter welchen Geschäftsbedingungen dieser für ihn die galvanische Vervielfältigung von Kupferplatten übernehmen würde.[44] Im gleichen Jahr meldete sich der „Kunstverein für die Rheinlande und Westphalen“. 1829 gegründet, war dies einer der ältesten Kunstvereine im deutschen Sprachraum. Seine Mitglieder schickten den Kupferstecher Josef von Keller nach Rom, um im vatikanischen Palast die Raphaels

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[40] Allgemeines Wiener Polytechnisches Journal, 18.4.1843, S. 368.
[41] TMW Archiv: Schreiben an Theyer und Waidele; Berlin, 21.5.1843.
[42] TMW Archiv: Klotz an Theyer; Halle, 3.11.1843.
[43] Franz von Kobell: Über die Fortschritte und den gegenwärtigen Stand der Galvanographie, in: Kunstblatt, Beilage zu den Wiener Sonntagsblättern, 22.10.1844, S. 353-355, das Zitat S. 355.
[44] TMW Archiv: Brockhaus an Theyer und Waidele; Leipzig, 11.6.1844.

„Disputa“ zu zeichnen und großformatig in Kupfer zu stechen. Dafür benötigte der Künstler zwölf Jahre, was den Verein 25.000 Taler kostete.[45] In der Folge diskutierten die Mitglieder über eine Vervielfältigung als Vereinsgabe, wobei sie zwischen Stahlstich und Kupferstich schwankten. Daher wurde Theyer angefragt, ob er die galvanoplastische Anfertigung von Platten übernehmen würde; er habe aber eine Erfolgsgarantie zu leisten.[46] Der Düsseldorfer Buch- und Kunsthändler Julius Buddeus erläuterte dazu, die teure Originalplatte müsse unbedingt unbeschädigt bleiben. Buddeus kontaktierte Theyer auch wegen eines anderen Bildes für den Kunstverein.[47] 1845 nahm darüber hinaus der Nürnberger Albrecht-Dürer-Verein Kontakt zu Theyer auf und ersuchte ihn um die galvanoplastische Reproduktion eines Kupferstichs von Albert Christoph Reindel nach der „Madonna“ Leonardo da Vincis.[48]

In Paris fand die Galvanotechnik besondere Verbreitung. Theyer sandte an die dortige Akademie der Wissenschaften einige Proben zur Galvanoplastik. Diese bedankte sich dafür in einem teilweise vorgedruckten Standardschreiben; es war vom prominenten Physiker und Politiker Dominique François Jean Arago unterschrieben. Er hatte sich in der Akademie u.a. für die fotografische Technik Louis Daguerres eingesetzt.[49] In der französischen Hauptstadt zeigten sich außerdem die Kunstverleger Adolphe Goupil, Théodore Vibert und Henri Rittner an einer Zusammenarbeit mit Theyer interessiert.[50]

Im russischen Reich war weiterhin Moritz Hermann von Jacobi, der Erfinder der Galvanoplastik, tätig. Er äußerte sich in der deutschsprachigen „St. Petersburger Zeitung“ über die Entwicklung seiner Technik und meinte: „Auch in Wien wird die Galvanographie lebhaft cultivirt und hat schon recht schöne Producte geliefert; welche besonders das Eigenthümliche haben, daß sie dieser Kunst rein angehören, und daß bei ihnen von der Benutzung anderer

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[45] Otto Ruhnke: Zur Feier des fünfzigjährigen Bestehens des Kunstvereins für die Rheinlande und Westfalen. Düsseldorf 1879, S. 16.
[46] TMW Archiv: Verwaltungsrat des Kunstvereins für die Rheinlande und Westphalen an Theyer; Düsseldorf, 14.10.1844.
[47] TMW Archiv: Buddeus an Theyer; Düsseldorf, 24.11.1844.
[48] TMW Archiv: Direktorium des Albrecht-Dürer-Vereins an Theyer; Nürnberg, 11.10.1845, 24.10.1845, 11.12.1845, 16.1.1846.
[49] TMW Archiv: Académie Royale des Sciences an Theyer; Paris, 4.3.1844.
[50] TMW Archiv: Goupil & Vibert an Theyer; Paris, 9. 8. 1844; Rittner & Goupil an Theyer; Paris, 18.8.1845.

Hülfsmittel, bis jetzt abstrahirt worden ist."[51] Theyer und Waidele sandten ferner Galvanografien an Maximilian Josèph Napoléon de Beauharnais, Herzog von Leuchtenberg, in St. Petersburg; dieser war sowohl mit Napoleon Bonaparte als auch mit der bayerischen Königsfamilie verwandt und mit einer Tochter des russischen Zaren verheiratet. Er befasste sich ausführlich mit der Galvanotechnik seiner Zeit und war damit wahrscheinlich der ranghöchste adelige Dilettant in dieser Branche. Bei Theyer ließ er sich über den Umweg des russischen Departements der Manufakturen bedanken.[52]

Erinnerung löschen. Die Übernahme des Betriebs durch die österreichische Hof- und Staatsdruckerei

Mehrere Beschriftungen zu den Archivalien im Besitz des TMW nennen als Zeitraum für das Bestehen des „galvanoplastisch-artistischen Laboratoriums" die Jahre von 1839 bis 1851. Bereits mit Ende des Jahres 1845 verschwinden aber die heute im Archiv vorhandenen, von Theyer gesammelten Zeugnisse über den Betrieb. In einem der letzten Dokumente bestätigte der Wiener Kupferstecher Leopold Beyer den Erhalt einer Summe für einen Stich, der für die Neujahrs-Enthebungskarte 1846 bestimmt war.[53] In diesem Jahr übernahm außerdem Franz Theyer die Handlung von seinem Vater Martin auf eigene Rechnung.[54] Dies mag ihn von weiterem Engagement für die Galvanografie abgehalten haben. In den folgenden beiden Jahren wurde die Habsburgermonarchie außerdem von einer schweren Wirtschaftskrise erfasst. Und auch während der revolutionären Aufstände 1848 und 1849 war mit Reproduktionen von Werken der bildenden Kunst wenig Geschäft zu machen. In welchem Jahr der Betrieb verschwand, bleibt unklar. Jedenfalls stellt sein Verschwinden und die Erinnerung an seine Existenz ein weiteres bemerkenswertes Kapitel dar, das hier kurz geschildert werden soll.

Die frühen Elektrochemiker waren auf Batterien als Stromquellen angewiesen. Erst die Entwicklung dynamoelektrischer Maschinen ermöglichte eine kontinuierliche Stromversorgung. 1867 erregte Werner Siemens auf der Weltausstellung in Paris großes Aufsehen mit einem

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[51] TMW Archiv: St. Petersburger Zeitung 1845, Nr. 9.
[52] TMW Archiv: Schreiben an Theyer; St. Petersburg, 26.4.1845.
[53] TMW Archiv: Beyer an Theyer; Wien, 9.10.1845.
[54] Theyer, siehe Anmerkung 1, S. 44.

solchen Generator. 1873 fand eine weitere Weltausstellung in Wien statt, wo u.a. erneut die Fortschritte der Elektrotechnik zur Schau gestellt wurden. Anlässlich dieses Ereignisses erschien eine zweibändige Darstellung über österreichische Beiträge zur Entwicklung der Produktion und Technik. Dort verfasste der Wiener Physiker und Fotograf Anton Martin einen Aufsatz über die Fotografie. Dabei kam er kurz auf Franz Theyer zu sprechen und erinnerte sich, dass er mit diesem gemeinsam Studien zur Fotografie betrieben hatte. Er erwähnte auch das Atelier, dessen aktive Zeit er auf die Jahre 1843 bis 1845 beschränkte. Martin schilderte, wie Theyer seine vielen Verbindungen zur Künstlerwelt nutzte, um Interesse für die Galvanografie zu wecken. Dafür habe er 30.000 bis 40.000 Gulden investiert; doch habe lediglich die Galvanoplastik diese frühe Zeit überlebt. Ein kurze Bemerkung Martins an dieser Stelle lässt aufhorchen. Er schrieb: „Theyer hat sich mit tüchtigen Kräften […] umgeben, und wenn er seine Anstalt eingehen liess und seine Platten vernichtete, so war er dazu nicht etwa durch die verlornen Geldopfer oder durch das Misslingen seiner Versuche veranlasst, sondern persönliche Motive, deren Erörterung nicht hieher gehört, hatten ihm die Sache verleidet.“[55]

Es sollte mehr als ein weiteres Jahrzehnt vergehen, bis der Schleier, der über diesen Andeutungen lag, öffentlich gelüftet wurde. 1883 fand in Wien eine große Ausstellung über Elektrotechnik statt, zu der ein umfangreicher Bericht erschien. Darin befasst sich der Elektrochemiker Richard Reuter mit der Galvanoplastik.[56] Einige Zeit später hielt Reuter im Niederösterreichischen Gewerbeverein einen Vortrag zu diesem Thema. Erst im Anschluss daran erfuhr er von der Existenz der Firma Theyer und Waidele, und zwar u.a. von Theyers Sohn Theodor, der ihm eine Reihe von Dokumenten aus Familienbesitz zur Verfügung stellte. Diese Unterlagen und Informationen ermöglichten Reuter eine ausführlichere Darstellung der Betriebsgeschichte. An Künstlern habe Theyer u.a. Karl Brocky, Peter Fendi, Josef von Führich, Karl Goebel, Wilhelm (?) Koller, Alois Petrak, Karl Rahl, Johann Matthias Ranftl, Wilhelm Richter, Karl von Saar, Karl Schindler, Anton Schrödl, Franz (Wilhelm?) Steinfeld und Albert Theer gewonnen. Er nannte zwei Standorte des Ateliers, nämlich am Josefstädter Glacis Nr. 215 sowie anschließend in einem angekauften Haus in der Bognergasse in St. Veit

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[55] Anton Martin: Photographie, in: Wilhelm Franz Exner (Red.): Beiträge zur Geschichte der Gewerbe und Erfindungen Oesterreichs von der Mitte des XVIII. Jahrhunderts bis zur Gegenwart. 2 Bände. Wien 1873. Band 1, S. 512-530, hier S. 524.

[56] Richard Reuter: Die Galvanoplastik, in: Niederösterreichischer Gewerbe-Verein (Hg.): Bericht über die internationale elektrische Ausstellung Wien 1883. Wien 1885, S. 161-180.

(heute Kremsergasse in Hietzing – Unter St. Veit), wo aufwändige unterirdische Heizungsanlagen für die galvanischen Bäder errichtet wurden. Dazu schrieb Reuter: „Theyer & Waidele sahen schon damals ein, dass vor Allem richtige Herstellung und Behandlung der Bäder, geeignete Temperatur derselben, übereinstimmendes Flächen-Verhältnis der Elektroden bei zweckmässiger Anordnung derselben, möglichst constante Stromstärke u. dergl. mehr, nothwendige Grundbedingungen sind, um gute Resultate erzielen zu können.“[57] Reuter erwähnte Schreiben an Theyer auch aus London und Rom und schätzte, das der Betrieb drei Jahre lang staatliche Unterstützung erhalten habe; darüber hinaus habe man eine Übernahme in Staatsbesitz unter Beibehaltung der Leitung durch Theyer und Waidele angekündigt. Dies habe gänzlich deren Wunsch entsprochen, da das Unternehmen zu diesem Zeitpunkt mit Verlust gearbeitet habe.[58]

Eine Übernahme im gegenseitigen Einverständnis wurde aber verhindert, und zwar durch niemand Geringeren als Alois Auer, den Leiter der staatlichen Hof- und Staatsdruckerei. Reuter schilderte in drastischen Worten die Ereignisse, wie sie ihm zugetragen worden waren: „Auer wusste es so zu veranstalten, dass das mit den Herren Theyer & Waidele so gut wie abgemachte Uebereinkommen (ihr Geschäft nämlich der Staatsdruckerei einzuverleiben) rückgängig gemacht wurde und errichtete mit Umgehung dieser Herren, aber mit Benützung der von ihnen gemachten Erfahrungen Hals über Kopf eine Abtheilung für Galvanoplastik in der Staatsdruckerei, in welcher selbstverständlich alle verwandten Zweige geübt werden sollten. Er stellte die Uebernahme der Einrichtung des in St. Veit etablirten Etablissements als vollkommen überflüssig hin und erklärte auch auf die Mithilfe oder Thätigkeit der Chefs dieses Geschäftes vollständig zu verzichten. […] Gerüchtweise wurde es auch offenkundig, dass Auer die Abwesenheit Theyer’s und Waidele’s benützt haben solle (denn ihre Beziehungen zum Auslande machten oft eine längere Abwesenheit von Wien nothwendig), um ihrer Anstalt Besuche abzustatten, um sich über Alles aufs Genaueste zu informiren. Thatsache ist es, dass Auer den Werkführer Theyer’s und Waidele’s, sowie ihren Kupferdrucker kaperte – oder wenn sie wollen, acquirirte – Männer, die nicht nur über Alles wohl informirt,

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[57] Richard Reuter: Die erste Anwendung der Galvanoplastik zum Zwecke der vervielfältigenden Künste. Separat-Abdruck aus der „Wochenschrift des Niederösterreichischen Gewerbevereines“. Wien 1886, S. 9.
[58] Ebd., S. 10, S. 15 f.

sondern von den Chefs auch abgerichtet waren, die alle Geheimnisse und Geschäfts-Vortheile kannten.“[59]

Reuter bemühte sich in seinem Vortrag durchaus um ein differenziertes Bild von Auers Charakter; er bescheinigte ihm Fleiß, Ausdauer und organisatorisches Talent. Auf der anderen Seite sei dieser ein Despot gewesen und habe wenig Skrupel gezeigt, seine Ideen durchzusetzen. Jedenfalls habe sein Vorgehen gegenüber Theyer und Waidele verheerende Folgen gezeigt, indem „in Folge aller dieser Vorgänge Waidele’s Sinne sich umnachtetet und er, so wie es heisst, in einer Irrenanstalt sein Dasein endete. Theyer hatte nur mehr einen Gedanken, den er aber mit der ihm eigenthümlichen Energie auch ausführte, nämlich Alles, was ihn im Entferntesten an die von ihm eingeführte und lieb gewonnene Galvanographie, an sein galvanoplastisches Atelier überhaupt erinnern könnte, zu vergessen – Haus und Einrichtung wurden verkauft, Vieles vernichtet, um nicht in unberufene Hände zu fallen, ja seine Erbitterung war so gross, dass die Kupferplatten […], die Matrizen, an deren Anfertigung so grosse Mühe und Sorge hing, an deren Herstellung so manche schlaflosen und kummervollen Nächte klebten, dass die Platten, die soviel Opfer an Zeit und Geld gekostet, den Weg in die Münze wanderten, um dort als Kupfer eingeschmolzen zu werden.“

Laut Reuter hatte Theyer lediglich einige Sach- und schriftliche Zeugnisse zwischen zwei versperrten Türen aufbewahrt, wo sie erst nach seinem Tod gefunden wurden. Ergänzend zu seinem Vortrag wurden Abdrücke galvanoplastischer Reproduktionen von Kupferstichen, Radierungen und galvanographischen Platten gezeigt. Reuter kam zu dem doch recht harschen Schluss: „Ich erblicke in dem Vorgehen Auer’s gegen Theyer & Waidele eine Bemächtigung der mit schweren Opfern gemachten Erfahrungen letzterer Herren.“[60]

Einige Jahre später überließ Theodor Theyer die Reste der galvanoplastischen Sammlung seines Vaters dem Technologischen Gewerbemuseum in Wien. Anlässlich dieser Übergabe

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[59] Ebd., S. 15-17, das Zitat S. 16.
[60] Ebd., S. 20 f, die Zitate S. 20, S. 21. Ob Waidele nach dieser Affäre wirklich in einer Irrenanstalt landete, ist nicht geklärt: Jedenfalls verließ er 1851/52 das Polytechnische Institut auf und trat einen Dienst in der Telegrafendirektion an: Faber, siehe Anmerkung 24, S. 26.

schrieb Richard Reuter erneut einen Beitrag, in dem er aus den bestehenden Quellen zur Geschichte des Unternehmens zitierte und im Großen und Ganzen seine früheren Ausführungen wiederholte.[61]

Wie ist diese handstreichartige Übernahme der galvanoplastischen Anstalt nun im historischen Rückblick zu bewerten? Alois Auer (1813-1869), der aus einfachen Verhältnissen stammte, machte die österreichische Hof- und Staatsdruckerei zu einem international sehr angesehenen Institut, wobei er seine eigenen Verdienste gerne betonte. Im Gegenzug lässt sich belegen, dass er die Erinnerung an Theyer und Waidele von Anfang an systematisch auslöschte. So publizierte Auer 1851 anonym eine Geschichte der Staatsdruckerei. Darin erwähnteer zwar die Abteilung für Galvanoplastik und die Galvanografie, aber ohne Hinweis auf deren Vorläufer. Die Druckerei war auch auf der ersten Weltausstellung in London vertreten und zeigte dort u.a. Produkte der Galvanoplastik.[62] Anfang Februar 1853 hielt Auer im Niederösterreichischen Gewerbeverein einen Vortrag über die technischen Einrichtungen des Unternehmens, der in Druck gelegt wurde. Ein ähnliche Fassung erschien noch im gleichen Jahr als Monografie. In beiden Fällen erhielt die Galvanoplastik erneut eine ausführliche Würdigung, ohne dass die Namen der Pioniere dabei zur Sprache kamen.[63]
Auf der zweiten Weltausstellung 1855 in Paris war die österreichische Staatsdruckerei erneut vertreten. In ihrem Verlag erschien auch ein Bericht über diese Schau. Ausführlich wurden u.a. die Produkte der westeuropäischen Konkurrenten geschildert, darunter jene von Charles Christofle in Paris sowie von Elkington und Mason in Birmingham. Besondere Aufmerksamkeit galt wiederum der Beschreibung der eigenen Erzeugnisse, deren Zahl sich auf über 300

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[61] Richard Reuter: Die Anfänge der Galvanographie und Galvanoplastik in Österreich, in: Mittheilungen des k.k. Technologischen Gewerbe-Museums, Section für Metall-Industrie und Elektrotechnik 5/56 (1889), S. 113-126.
[62] Geschichte der k.k. Hof- und Staatsdruckerei zu Wien. Wien 1851, S. 30-33. Im Anhang: Übersicht der von der Wiener k.k. Hof- und Staatsdruckerei in London ausgestellten Gegenstände aller graphischen Kunstzweige.
[63] Alois Auer: Über den polygraphischen Apparat der k.k. Hof- und Staatsdruckerei in Wien, in: Verhandlungen des niederösterreichischen Gewerbe-Vereins. Neue Folge 1853, S. 52-87, hier S. 67-71; Ders.: Der polygraphische Apparat oder die verschiedenen Kunstfächer der k. k. Hof- und Staatsdruckerei zu Wien. I. und II. Vortrag: Die Erklärung und praktische Anwendung des polygraphischen Apparates. Wien 1853, S. 33-37.

belief. Für ihre gesamten Leistungen erhielt die Druckerei eine große Ehrenmedaille verliehen.[64]

Auch in einer späteren Erinnerungsschrift an seine Dienstzeit erwähnte Alois Auer – nunmehr Ritter von Welsbach – Theyer und Waidele mit keinem Wort. Dagegen führte er einen Streit um eigene Prioritätsrechte an, der ihn damals stark beschäftigt hatte. 1852 ließ er über Andreas Worring, einen Faktor der Hof- und Staatsdruckerei, die Erfindung des sogenannten Naturselbstdrucks zum Patent anmelden. Im Jahr darauf wurde diese zur allgemeinen Nutzung freigegeben, und Auer veröffentlichte eine Schrift dazu. Darin zog er scharf gegen Henry Bradbury zu Felde, der angeblich seine gastfreundliche Auskunftswilligkeit ausgenutzt und dann in England seine Priorität angezweifelt hatte.[65] Beim Naturselbstdruck wurde eine Pflanze, ein Insekt oder ein anderer Gegenstand zwischen eine Stahl- und eine Bleiplatte gelegt und dann gepresst, wobei sich auf dem weichen Blei ein Negativabdruck abzeichnete. Dieser wurde dann galvanoplastisch abgenommen und konnte anschließend vervielfältigt werden. Henry Bradbury (1831-1860) hatte das Verfahren in Wien kennengelernt und es sich in England patentieren lassen. Möglicherweise führte der Streit mit Auer um die Priorität der Erfindung zu seinem frühen Tod.[66] In jedem Fall zeigt dieser Konflikt, dass Auer seinerseits mit Gegenspielern, die sein geistiges Eigentum in Frage stellten, wenig zimperlich verfuhr.

Die Objekte: ein Befund aus naturwissenschaftlich-konservatorischer Sicht

Der eingangs erwähnte, bei der Depotinventur des Technischen Museums Wien wiederentdeckte hölzerne Schrank und sein Inhalt sind Gegenstand einer Dissertation, die derzeit von Valentina Ljubić Tobisch vorbereitet wird. Die Objekte werfen eine Reihe von Fragen auf und lassen viel Raum für Untersuchungen, aber auch für Spekulationen offen. Aus einem Schreiben von Johann Schwerdtner vom 12.5.1917 an die Galvanoplastische Abteilung des Technischen Museums für Industrie und Gewerbe geht hervor, wer für die Entstehung des

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[64] Eberhard A. Jonák (Red.): Bericht über die allgemeine Agricultur- und Industrie-Ausstellung zu Paris im Jahre 1855. Band 1. Wien 1857-1858, S. 34-40.
[65] Alois Ritter Auer von Welsbach: Mein Dienstleben. Verkürzter Neudruck der vom Finanzministerium 1864 unterdrückten Original-Ausgabe. Hg. von Rudolf Payer-Thurn. Wien, Leipzig 1923, S. 43 f.
[66] Rolf H. Krauss: Fotografie und Auers Natur-Selbstdruck. Kontaktbilder als Medien einer mechanischen Objektivität, in: Fotogeschichte 31/121 (2011), S. 13-24, hier S. 16 f, 19 f.

Schranks verantwortlich war. Schwerdtner schrieb: „Herr Theodor Theyer hat bei Gründung des Arbeitsmuseums in der Währingerstrasse des technologischen Gewerbemuseums in lichtem Holz einen Kasten im Renaissance-Stile, gezeichnet von Leopold Theyer, dem Architekten u. Baurat, zeichnen u. ausführen lassen, um die von seinem Vater erfundene Galvanographie im Museum auszustellen. Das war eine mißlungene Idee, die vorhandenen Abdrücke in großer Zahl in einen Kasten zu versperren und eigentlich einzusargen. Das Technische Museum hat u. a. eine Abteilung für Galvanoplastik ins Leben gerufen und es ist daher naheliegend, daß ich der von der ganzen Sache weiß und die Entstehung der Bilder und Kupferplatten gesehen hat, und so glücklich war, die auf den Bildern entstehende Schrift auf den Kupferplatten gestochen zu haben, mich um die Sache annehme und dieselbe der Öffentlichkeit nicht vorenthalte.“ Schwerdtner bezeichnete weiters das Verfahren als eine „epochemachende Erfindung“ und hielt es für die Pflicht des Museums, dieser speziell österreichischen Erfindung einen Ehrenplatz unter den graphischen Künsten zu erteilen.[67, 68]

Es konnte bis jetzt nicht in Erfahrung gebracht werden, ob Theyers Produkte ihren Platz in der damals neukonzipierten Ausstellung des Technischen Museums gefunden haben. Der von Schwerdtner beschriebene Schrank, beherbergte bei seiner Auffindung 2008 insgesamt 217 ordentlich sortierte und nummerierte graphische Drucke sowie 73 Metallarbeiten. Anhand von Fehlstellen auf den Objektträgern war ersichtlich, dass einige Stücke fehlen. Auf der Innenseite der Schranktür klebt eine kleine Nummer 2 und lässt das Bestehen eines weiteren Schranks möglich erscheinen.

Eine der zentralen Fragen, die mit diesen Objekten in Verbindung gebracht werden, ist, welche detaillierten Herstellungsverfahren verwendet wurden. Eine genaue Zuordnung der Techniken ist noch nicht bei allen Papier- und Metallarbeiten eindeutig möglich[69], es konnte nur eine erste Gruppierung vorgenommen werden. Bei den Graphiken handelt es sich um Abdrücke, deren Druckplatten nach drei bis jetzt bekannten Methoden hergestellt wurden:

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[67] TMW Archiv, Frühakten, Mappe 69/XI.

[68] Johann Schwerdtner hielt 1886 als Mitglied des Niederösterreichischen Gewerbeverein im Graphischen Club einen Vortrag über die Verdienste Theyer’s und Waidele’s auf dem Gebiete der Galvanographie. Nach Reuter, siehe Anm. 56, S. 23.

[69] In der folgenden Arbeit wird näher auf die Metallgegenstände eingegangen. Vollständigkeitshalber werden die gedruckten Blätter immer wieder erwähnt.

galvanoplastische Reproduktionen von Kupferstichplatten, von Radierungen und von galvanographischen Platten[70].
Die angewandten Techniken bei den Metallgegenständen können nach der ersten optischen Beurteilung wie folgt angegeben werden: galvanoplastische Reliefs aus Kupfer, galvanische Kopien von gestochenen Kupferplatten, galvanische Kopien von original radierten Kupferplatten, mit Elektrotinte erzeugte Kupferplatten (Galvanographien) und galvanisch hergestellte und fotografisch belichtete Kupferdruckplatten, geätzt.

Die Metallarbeiten unterscheiden sich in Größe, Form, Materialbeschaffenheit und Qualität der Ausführung. Ungefähr ein Drittel der Gegenstände trägt einen deckenden Überzug aus Gold oder Silber. An manchen anderen Platten können partiell Spuren metallischer Beschichtungen erkannt werden. Diese werden aber mehr in Verbindung mit dem Herstellungsprozess gebracht und nicht als dekorativer Edelmetallüberzug in Betracht gezogen. Einige Motive stimmen mit den vorgefundenen Drucken überein. Die Kanten der Druckplatten wurden sorgsam mit einer feineren Feile geebnet und die Ecken abgerundet, die narbigen Gebilde aus dem galvanischen Bad auf der Rückseite der Platten mit einer groben Feile entfernt und die Rückseiten geebnet.

Wie bereits Kobell in München beobachtete, konnte das Kupfer über die leitenden Flächen hinaus auf die nichtleitenden galvanisch abgeschieden werden. Dadurch gelang es ihm, bemalte Kupferplatten im galvanischen Bad genau zu kopieren. Die Herausforderung stellte die Beschaffenheit der Farbe und der zu benutzenden Trägerplatte dar, Techniken, die von Theyer und Waidele weiterentwickelt wurden. Die Farbe musste gut an der Platte haften bleiben und durfte vom galvanischen Bad nicht angegriffen werden. Je nachdem welche graphische Technik sie zu imitieren hatte, sollte sie matt oder glatt auftrocknen. Für einen matten Auftrag wurde die noch frische Farbe mit Graphit, Silberpulver oder anderen leitfähigen Partikeln bestäubt.

Richard Reuter beschreibt in seinem Vortrag im Niederösterreichischem Gewerbeverein 1886, den er mit Informationen von Franz Theyers Sohn Theodor vorbereitet hatte, welche

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[70] Reuter, siehe Anm. 56, S. 6.

anderen Farben verwendet wurden. Er schildert außerdem welche Details beim Malen eines Galvanographiebildes eine Rolle spielten und mit welchen Pigmenten gearbeitet wurde. So wurden u.a. Eisenoxyd, Ocker, Graphit, Rebenschwarz[71] mit in Terpentinöl und Dammarfirnis gelöstem Wachs verrieben und zum Malen verwendet. Pastösere, dickere Farbschichten wurden mit einem höheren Graphitzusatz leitend gemacht, während dünnere Farbaufträge, ohne besonders leitend gemacht zu werden, sich verhältnismäßig leicht und schnell mit Kupfer überziehen ließen[72]. Da die galvanogeformten Platten im Randbereich durch Überwachsen nichtleitender Bereiche an der Negativform hafteten, mussten sie von dieser getrennt werden. Die geschah vermutlich mechanisch, indem die Ränder entfernt wurden.

Gegenstände aus der frühesten Zeit der Galvanotechnik sind eine kulturhistorische Besonderheit und stellen eine Wissensgrundlage dieser heute noch industriell sehr wichtigen Technologie dar.[73] Die frühe Anwendung der Galvanoformung zur Herstellung von Druckplatten und anderen Gegenständen lag zum erheblichen Teil an hervorragenden mechanischen Eigenschaften von galvanisch abgeschiedenem Kupfer und der neuen Möglichkeit, Gegenstände perfekt kopieren und vervielfältigen zu können. Die neue Technik ermöglichte es auch, nichtleitende Materialien mit Metall zu überziehen sowie dünne und für die Gesundheit unschädliche Versilberungen und Vergoldungen durchzuführen. Die sich hierbei ergebenden Fragen und Problemstellungen sind insbesondere auf fehlende Kenntnisse ihrer Oberflächenbeschaffenheit sowie ihrer chemischen und morphologischen Zusammensetzung zurückzuführen.

Physikalisch-chemische Untersuchungen sollen Aufschlüsse über innere Struktur, Zusammensetzung und Herstellungsverfahren der Objekte bringen[74]. Die 73 Metallgegenstände aus dem Theyer'schen Laboratorium bedürfen außerdem erhaltender Maßnahmen, um wieder für Ausstellungen und Forschungszwecke zur Verfügung stehen zu können. Umfassende anwendungsorientierte Grundlagenuntersuchungen sollen zu einem genauen Verständnis der Kor-

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[71] Durch Verkohlung trockener Weinreben gewonnenes Schwarzpigment.
[72] Reuter, siehe Anm. 56, S. 21.
[73] Thomas Walter Jelinek: Praktische Galvanotechnik, 5. Auflage, Bad Saulgau 1997.
[74] Koen Janssens, René Van Grieken: Non-destructive Microanalysis of Cultural Heritage Materials. Amsterdam, 2004.

rosionsmechanismen führen und so eine rasche, zielorientierte Konservierung und Restaurierung ermöglichen. Solche Kenntnisse stellen die Grundlage für die Reinigungs- und Konservierungsstrategie dar und helfen bei der Entwicklung auf die einzelnen Objekte zugeschnittenen Restaurierkonzepte. Ein großer Wert soll dabei auf zerstörungsfreie Untersuchungsmethoden gelegt werden.

Nach jahrzehntelanger Lagerung der Inhalte im Holzschrank haben sich unterschiedliche Schäden eingestellt. Bei den Metallgegenständen können unterschiedliche Korrosionsphänomene von leichter Oxidbildung bis zu stärkerer Flecken- und Korrosionsbildung beobachtet werden. Die metallischen Überzüge sind teilweise sehr dünn und stellenweise mit Korrosion durchwachsen. Bei den Metallarbeiten aus Theyers Laboratorium soll ein besonderes Augenmerk auf die Versilberungen gerichtet werden. Einerseits sind die Silberbeschichtungen kaum nachgedunkelt. Diese Reaktionsträgheit vom Silber ist sehr untypisch, vor allem wenn man bedenkt, dass sich der Bestand lange in einem Holzschrank befand und Holz bekanntlich durch die Säureabspaltung rasche Oxidation der Metalle verursacht. Üblicherweise kommt es bei nicht geschützten Versilberungen zu einer schnellen Reaktion mit der umgebenden Luft[75]. Ein anderes interessantes Phänomen zeigt sich in der Art der Silberbeschichtungen. Sie sind teilweise beim gleichen Bild in unterschiedlicher Stärke aufgebracht und zeigen ein malerisches fast dreidimensionales Ergebnis. Durch die unterschiedliche Stärke der Versilberung scheint das rötliche Kupfer mehr oder weniger durch, beeinflusst die Farbigkeit und lässt glauben, dass es sich um eine Fotografie handelt.[76]

Da viele Oberflächendetails nicht mit dem bloßen Auge zu erkennen sind, wurde als erste Methode zur Untersuchung der Objekte die optische Mikroskopie herangezogen. Sie ist nach

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[75] Gerhard Schikora: Über die Korrosion von Metallen in hölzernen Gehäusen. Materials and Corrosion 12 (1961), S. 1-10.

[76] Lene Grinde: George Eastman House International Museum of Photography and Film & Image Permanence Institute, Rochester Institute of Technology, 11 July 2005. "Conservation of Stereo Daguerreotype: Examination and Documentation of the Characteristics". http://notesonphotographs.eastmanhouse.org/images/3/36/Lene_Grinde_for_web.pdf

wie vor unverzichtbar für die Untersuchung und Dokumentation von Oberflächenzuständen.[77] Darüberhinaus wurden Oberflächen unter dem Rasterelektronenmikroskop (REM)[78] untersucht und eine Elementanalyse mit Energiedispersiver Röntgenspektroskopie (EDX) vorgenommen. Diese liefert durch Elektronenbeschuss ausgelöste Röntgenemissionen, die durch ihre Frequenz Informationen über den elementaren Aufbau des Materials ermöglichen. Die Intensität der Röntgenstrahlung gibt einen direkten Hinweis auf die Austrittstiefe. Dadurch können Hinweise auf die Dicke von Deckschichten wie zum Beispiel von Oberflächenschmutz oder Korrosionsprodukten gewonnen werden. Und schließlich wurde die Stärke der Metallbeschichtung bei allen versilberten und vergoldeten galvanogeformten Objekten mit Hilfe der Röntgenfluoreszenzanalyse (RFA) untersucht. [79]

Um Informationen über (In-)Homogenität und reproduzierbare Werte zu bekommen, wurden die Metallbeschichtungen an mehreren Stellen gemessen und die Mittelwerte ausgewertet. Die unterste messbare Schichtstärke lag bei 0,03 µm.

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[77] Lichtmikroskop Olympus GX51 (Happy Plating GmbH). Die Autor/innen danken Herrn Dr. W. Hansal (Happy Plating GmbH) für sein großes wissenschaftliches Interesse und seine tatkräftige Unterstützung des Projektes durch die Ermöglichung zahlreicher instrumenteller Untersuchungen.
[78] Elektronenmikroskop Zeiss Supra 55 VP (Universität Wien, Fakultäten für Physik und Chemie)
[79] Röntgenfluoreszenzanalyse: Röntgenanalytik Messtechnik GmbH, maXXi 5 PIN (Happy Plating GmbH).

Abb. 2 Galvanografie (Nr. 234). Foto Peter Sedlaczek, Technisches Museum Wien

An Objektbeispielen sollen hier kurz die mit Elektrotinte erzeugten Kupferplatten vorgestellt werden. Die Differenzen im Glanz konnten auf das Vorhandensein von Kratzern, Korrosionsprodukten und anderen Oberflächenstörungen wie Schmutzpartikeln zurückgeführt werden. Allgemein ließ sich im Rasterelektronenmikroskop beobachten, dass nichtkorrodierte Oberflächen sehr dicht und glatt sind und die Rauheit meistens ein Anzeichen für die Schädigung der Oberfläche ist und nicht vom Herstellungsprozess stammt. Ausnahme sind Oberflächen, die nach der galvanischen Abscheidung geätzt wurden. Bei Druckplatten konnten dabei einige typische Herstellungsmerkmale erkannt und die Galvanographien von Stichen gut unterschieden werden. Beim Malen von den Galvanographiemotiven wurden unterschiedliche Malmittel verwendet, was die Struktur der Vertiefungen sehr gut widerspiegelt.

Tab. 1 Elementare Zusammensetzung der Oberfläche von Platte Nr. 234 nach der Atommasse (%)

Cu	6
C	46
O	42
Anorganische Bestandteile	5
Ag	1

Platte 234 zeigt in den abgeformten Vertiefungen relativ grobe Strukturen (Abb. 2). Die EDX-Elementaranalyse (Tab. 1) ergibt eine massive Bedeckung mit kohlenstoff-wasserstoff-haltigem Material. Dies wird plausibel durch ein schwaches Cu-Signal (6%) gegenüber den Elementen C, O und anderen, die eine Deckschicht über dem Kupfer bilden. Dies könnte auf einerseits natürliche Verschmutzung und andererseits Restbestandteile der Druckerfarbe zurückzuführen sein, die auch typischerweise anorganische Bestandteile (Na, K, Si, S etc.) aufweist. Bemerkenswert ist, dass auch eine Spur Silber (1%) vor allem in den Vertiefungen nachgewiesen werden kann, was die optische Beobachtung bestätigt (Abb. 3).

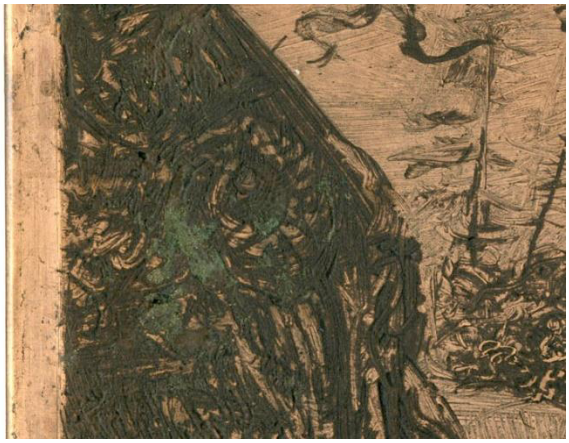

Abb. 3 Galvanografie (Nr. 234), Silberspuren in den Vertiefungen, Detailansicht. Foto: Peter Sedlaczek, Technisches Museum Wien

Diese Komponente kann auf den Prozess zur Leitfähigmachung der dickeren Farbbereiche durch aufgestreutes Silberpulver zurückgeführt werden.

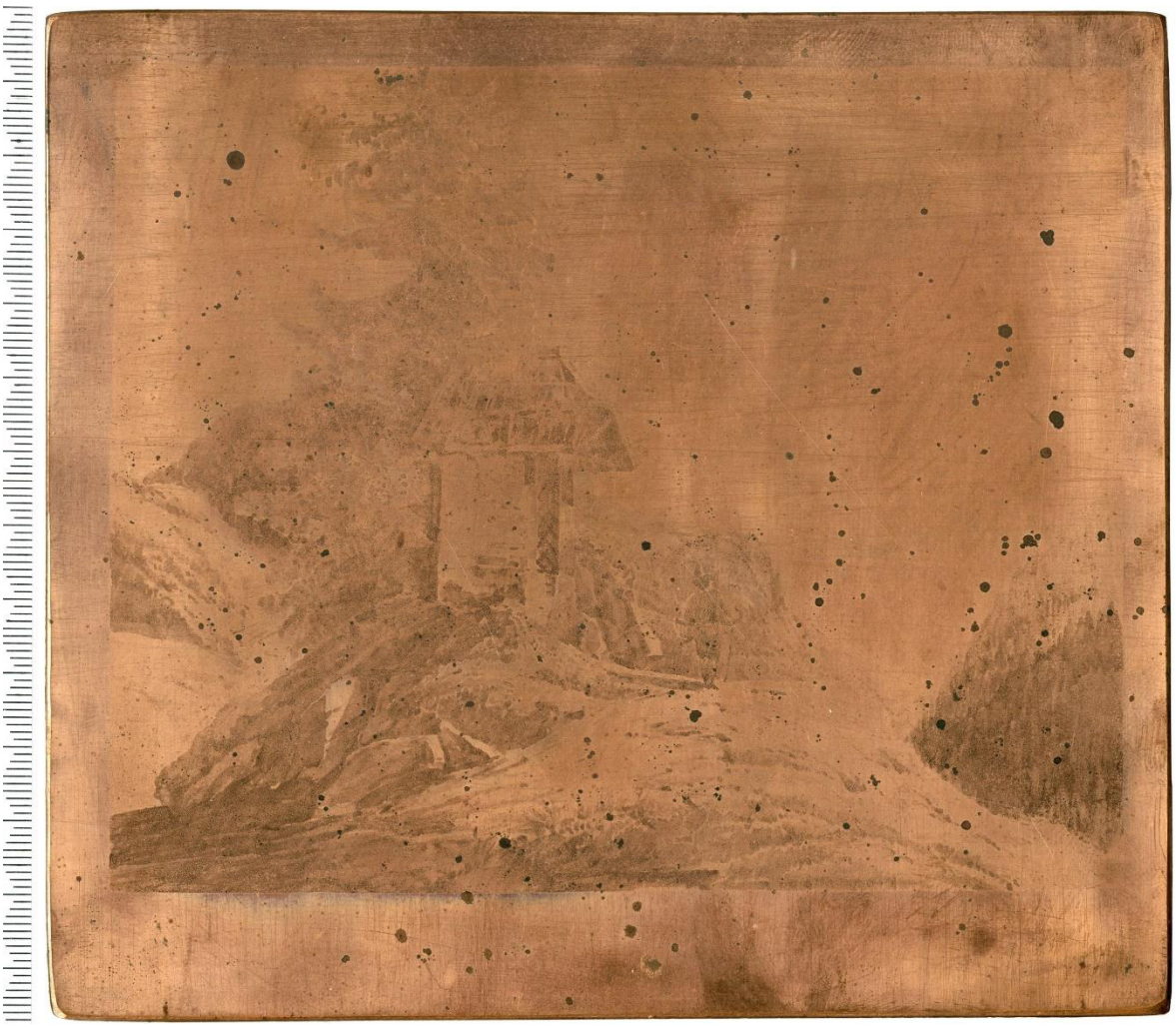

Abb. 4 Galvanografie (Nr. 222), Foto: Peter Sedlaczek, Technisches Museum Wien

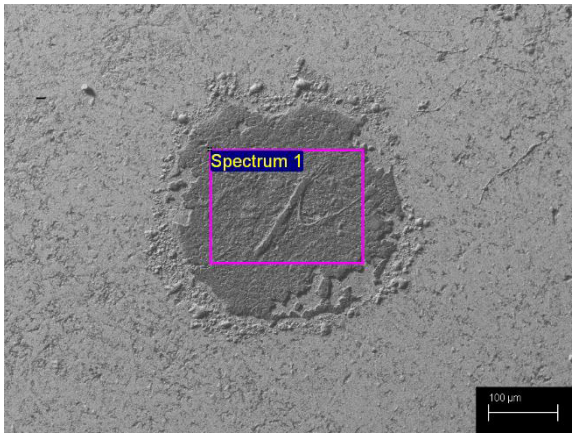

Abb. 5 Galvanografie (Nr. 222), Detail von einem Spritzer auf der Vorderseite, REM-Aufnahme

Die Platte 222 (Abb. 4) zeigt ein anderes Erscheinungsbild. Auf der Vorderseite befinden sich offenbar nachträglich aufgebrachte Spritzer (Abb. 5). Nicht kontaminierte Bereiche, die ursprünglich nur die Druckerschwärze aufgenommen haben, weisen Cu und C-O-Bestandteile auf, die Oxide bzw. Verunreinigungen andeuten (Tab. 2). Wesentlich ist, dass keine anorganischen Elemente nachgewiesen werden konnten, die allerdings auf den Spritzern vorliegen. Dort verringern sie den nachweisbaren Cu-Wert durch das Abdecken des Spritzermaterials. Offenbar deutet diese Zusammensetzung, wie sie im Bereich der Reste der Druckerschwärze in Probe 234 gefunden wurde, ebenfalls eher auf die Kontaminierung mit Druckerschwärze hin. So ist bei der Platte 234 eine sehr grobe (Abb. 6a) und bei der Platte 222 eine eher faserige (Abb. 6b) Struktur zu erkennen. Im Gegensatz dazu wirken die Motivrillen bei der Platte 226 sehr flach und porös (Abb. 6c) und unterscheiden sich von der dichten Struktur der umgebenden Partien. Dies könnte ein Hinweis auf eine Bearbeitung der Platte im zweiten Schritt sein, d.h. nach ihrer Herstellung im galvanischen Bad.

Tab. 2 Elementare Zusammensetzung der Oberfläche von Platte Nr. 222 nach der Atommasse (%)

Cu	4
C	56
O	36
Anorganische Bestandteile	4

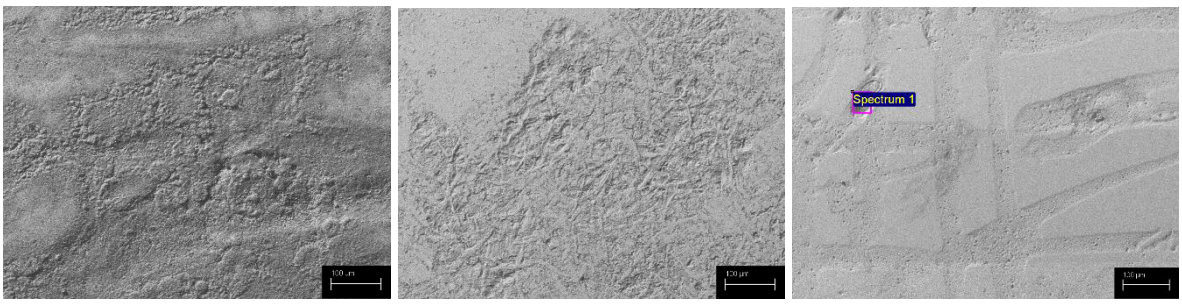

Abb. 6 a, b, c Details aus dem Motivberich der Platten (Nr. 234, 222 und 226), REM-Aufnahmen 2011

Die Sammlung enthält eine Reihe von galvanoplastischen Reliefs aus Kupfer mit Edelmetallüberzügen in der Form von Medaillons (Tab. 3 und 4). Bei der Betrachtung der Oberflächenstruktur unter dem Rasterelektronenmikroskop wurde sichtbar, dass die Bearbeitungsspuren

(Riefen) aus dem Herstellungsprozess der Negativ-Form in das galvanoplastische Abformungs-Positiv übertragen wurden. Die Ag- und Au-Schichtdicken wurden mittels RFA bestimmt. Sie variierten von nicht mehr messbaren Werten unter 30 nm bis zu 380 nm.
Der Korrosionszustand, also die Häufigkeit von lokalen Korrosionsausblühungen, kann bei Gold-beschichteten Objekten in erster Näherung mit der Dicke *d* korreliert werden. Objekte mit Beschichtungen über ca. 200 nm zeigen praktisch keine Veränderungen (Abb. 7). Die Anfälligkeit für Korrosion bei 40 nm Schichtdicke ist deutlich in Abb. 8 zu erkennen, da die Au-Schicht aufgebrochen und offenbar von einer Konversionsschicht aus dem Basismaterial überlagert wurde. Diese Bereiche besitzen eine deutlich geringere elektronische Austrittarbeit und erscheinen im Bild dunkler als die intakte Au-Schicht. Es kann angenommen werden, dass sich Kupferoxid aus den Bruchspalten des Goldes über die Deckschicht ausgebreitet hat. Die hellen Stellen in den aufgebrochenen Riefen der Goldschicht weisen auf ein Material hin, das sich unter Elektronenbeschuss stark auflädt, weil es die geringste Elektronenleitfähigkeit aller vorliegenden Phasen besitzt. Dabei könnte es sich um metallsalzhaltige Präzipitate handeln. Die Korrosionsanfälligkeit bleibt auch bei etwas größeren Schichtdicken bis über 70 nm erkennbar (Tab. 3). Es muß die Möglichkeit erwogen werden, dass in diesem Dickebereich von ca. 70 bis ca. 180 nm auch die Zusammensetzung der Beschichtung eine beschleunigende Wirkung aufweist. Tatsächlich treten mittlere bis starke Korrosionserscheinungen auf, wenn Quecksilberanteile im Gold nachgewiesen werden konnten (Tab. 3, Abb. 8).

Die silberbeschichteten Medaillons zeigen im beobachteten Schichtdickenbereich von 40 bis 140 nm relativ starke Korrosionserscheinungen (Tab. 4). Die Ag-Schicht wird stellenweise von Kupferkorrosionsprodukten aus dem Substrat heraus aufgebrochen, wobei kleine intakte Silberinseln bestehen bleiben. Signifikant erscheinen im REM helle Bereiche, die auf sich stark aufladende und daher elektronisch isolierende Substanzen hinweisen. Es wäre angesichts der optisch dunkel bis schwarz erscheinenden Korrosionsflecken naheliegend, diese isolierenden Phasen mit dem sehr unlöslichen Silbersulfid zu korrelieren (Abb. 10).

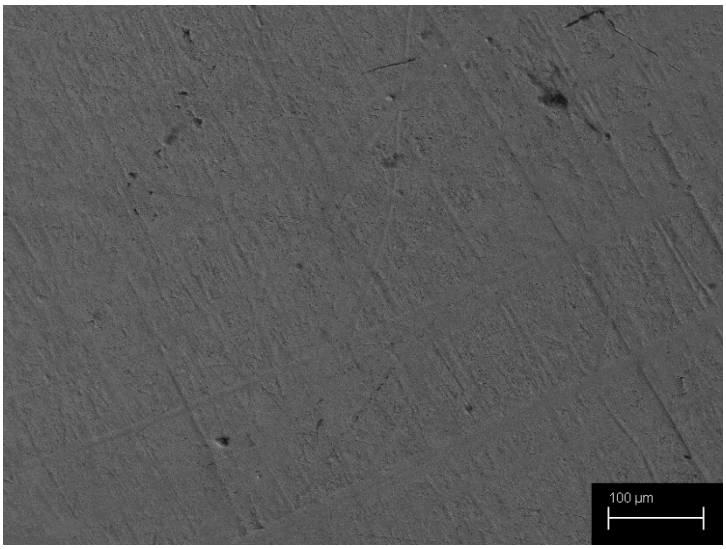

Abb. 7 Vergoldetes Medaillon (Nr. 284), Detail aus dem Halsbereich, Gold-Schichtdicke 380 nm, REM-Aufnahme, 2011.

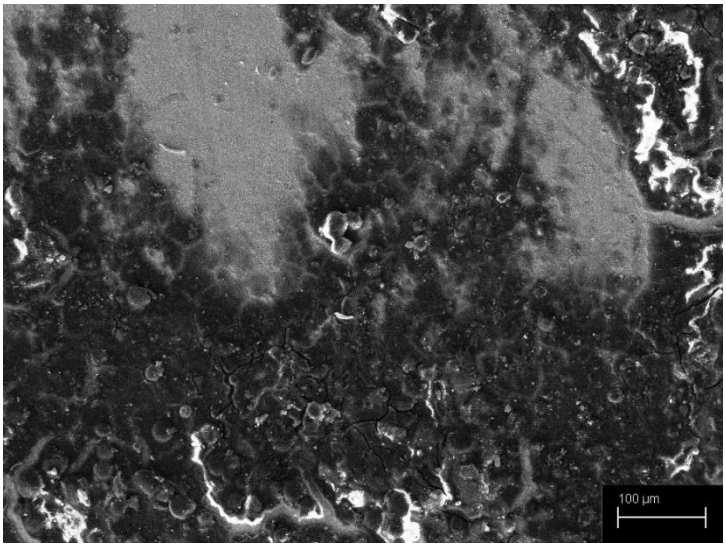

Abb. 8 Vergoldetes Medaillon (Nr. 291), Detail aus dem Hintergrund, Gold-Schichtdicke 40 nm, REM-Aufnahme, 2011.

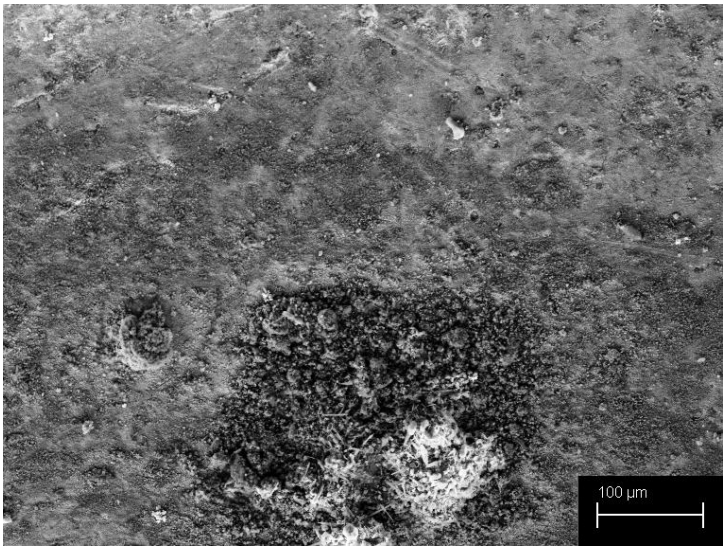

Abb. 9 Vergoldetes Medaillon (Nr. 282), Detail aus dem Hintergrund, Gold-Schichtdicke 180 nm, Quecksilberspuren (aus EDX-Analyse), REM-Aufnahme, 2011.

Tab. 3 Gold-Schichtdicken (*d*), Fotos: Peter Sedlaczek, Technsiches Museum Wien

	Nummer	*d* [nm]	Kommentar	Korrosionszustand
	254	380		gut
	284	230		gut
	282	180	Spuren von Hg (EDX)	stark
	281	140	Dunkler Spritzer mit Fremdmaterial (EDX: C, O, S)	mittel
	288	70	Spuren von Hg (EDX)	mittel
	285	70		gut, Korrosionsentwicklung nur an abgeriebenen Stellen
	283	40	Spuren von Hg (EDX)	stark
	291	40		stark

Tab. 4 Silber-Schichtdicken (*d*)

	Inv.-Nr.	*d* [nm]	Kommentar	Korrosionszustand
	269	140	Schichtdicke sehr inhomogen	stark
	265	60		stark
	294	40		stark

Für die endgültigen Bestimmung, mit welcher Technik und aus welchem Material die Metallobjekte aus dem Laboratorium von Franz Theyer hergestellt wurden, werden noch Forschungen durch Analysen, Recherchen und Abgleich mit anderen Objekten durchgeführt. Interessant ist die Tatsache, dass bei bisherigen Untersuchungen keine (organischen) Beschichtungen festgestellt wurden, das korrosive Verhalten der Objekte aber ganz unterschiedlich ist.

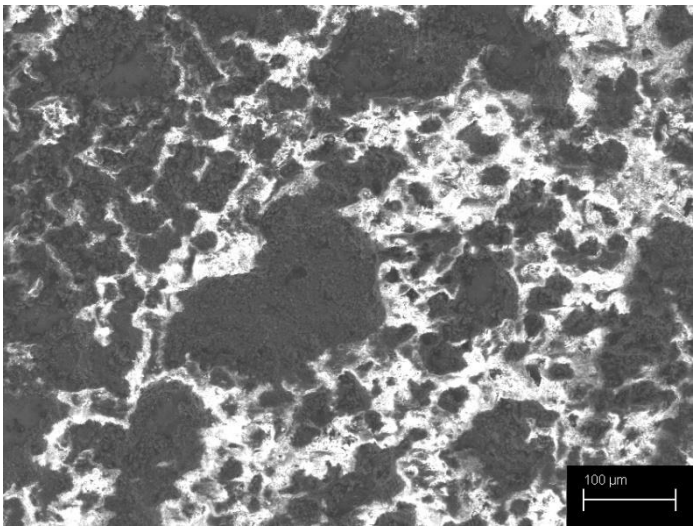

Abb. 10 Versilbertes Medaillon (Nr-265), Detail aus dem Randbereich, Silber-Schichtdicke 60 nm, REM-Aufnahme, 2011

Ziel weiterer Versuche wird es sein, Informationen über die innere Struktur der galvanisch hergestellten Gegenstände zu ermitteln. Dies ist einerseits für die Aufklärung der von Zeitgenossen so sehr geschätzten physikalischen Eigenschaften wichtig[80] und andererseits können diese Informationen eventuell mehr Aufschluss über die Korrosionsprozesse bringen.

Weiters sollen anwendungsorientierte elektrochemische Reinigungsmethoden[81] an den historischen Oberflächen getestet werden. Schwerpunkt ist die Entwicklung und Optimierung von Reinigungsverfahren und deren Anpassung an die konservierungsrelevanten Erfordernisse. Die Ergebnisse aus weiteren Untersuchungen werden an anderer Stelle veröffentlicht.

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[80] Siehe Absatz „Das „galvanoplastisch-artistische Laboratorium“ von Theyer und Waidele in Wien“.
[81] C. Degrigny, Journal of Solid State Electrochemistry 14, 2010, S. 353–361.

Appendix II

Auszug aus den Objektdatenblättern des Technischen Museum Wien ergänzt durch REM, EDX und lichtmikroskopische Aufnahmen

Im Rahmen dieser Arbeit wurde eine große Menge an wissenschaftlichen Daten und Ergebnissen generiert. Um sie für die weitere Forschung zu erhalten, wurden sie in die Objektdatenbank des Technischen Museums Wien aufgenommen. Aufgrund der großen Datenmenge werden alle Ergebnisse in Kurzform zu dem vorliegenden Anhang hinzugefügt. Weitere Fachpublikationen sind geplant.

Inventarnr.: 83939/1 **Alte Inventarnr.:** MdA4, 219

Sammlungsgr.: 530 Metallbearbeitung

akt. Standort: Standorte-TMW/TMW-Museum/E5/3-102

Titel: Kupferdruckplatte

Hersteller_in: Theyer, Franz; Waidele, Erwin

Ort: Wien

Datierung: 1840 **bis** 1845

Maße:

Breite 10.8 cm

Tiefe 14.2 cm

Höhe 0.1 cm

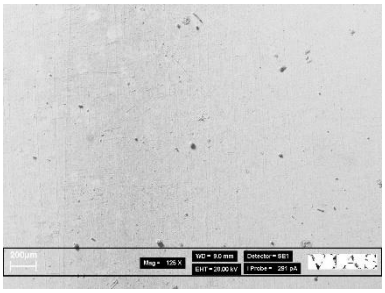
Beschreibung:

Befindet sich in Lade 4 (von oben gezählt) auf der mit schwarzem Stoff bespannten Tafel (dort befinden sich die Nummern 219-226, 228-235 und darunter 48).

Schlagworte: Kupfer

Digitalverweise:

REM, EDX (Zeiss EVO 60 XVP, Universität Wien)



Element	Atomic%	Element	Atomic%	Element	Atomic%
C	64.54	C	59.89	C	63.76
O	13.66	O	15.46	O	18.29
S	0.24	Cu	24.58	Si	0.30
Co	0.01	Pb	0.06	S	0.27
Cu	21.56			Cu	17.38

Lichtmikroskopaufnahmen (z-Scans; Keyence, VHX-5000), Universität für Bodenkultur Wien

Inventarnr.: 83939/2 **Alte Inventarnr.:** MdA4, 220

Sammlungsgr.: 530 Metallbearbeitung

akt. Standort: Standorte-TMW/TMW-Museum/E5/3-102

Titel: Kupferdruckplatte

Hersteller_in: Theyer, Franz; Waidele, Erwin

Ort: Wien

Datierung: 1840 **bis** 1845

Maße:

Breite 14.5 cm

Tiefe 13.6 cm

Höhe 0.1 cm

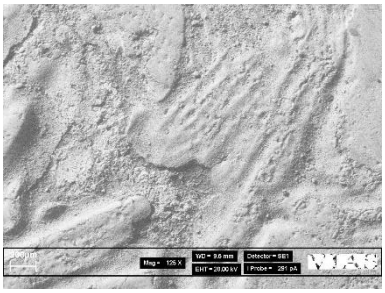
Beschreibung:

Befindet sich in Lade 4 (von oben gezählt) auf der mit schwarzem Stoff bespannten Tafel (dort befinden sich die Nummern 219-226, 228-235 und darunter 48).

Schlagworte: Kupfer

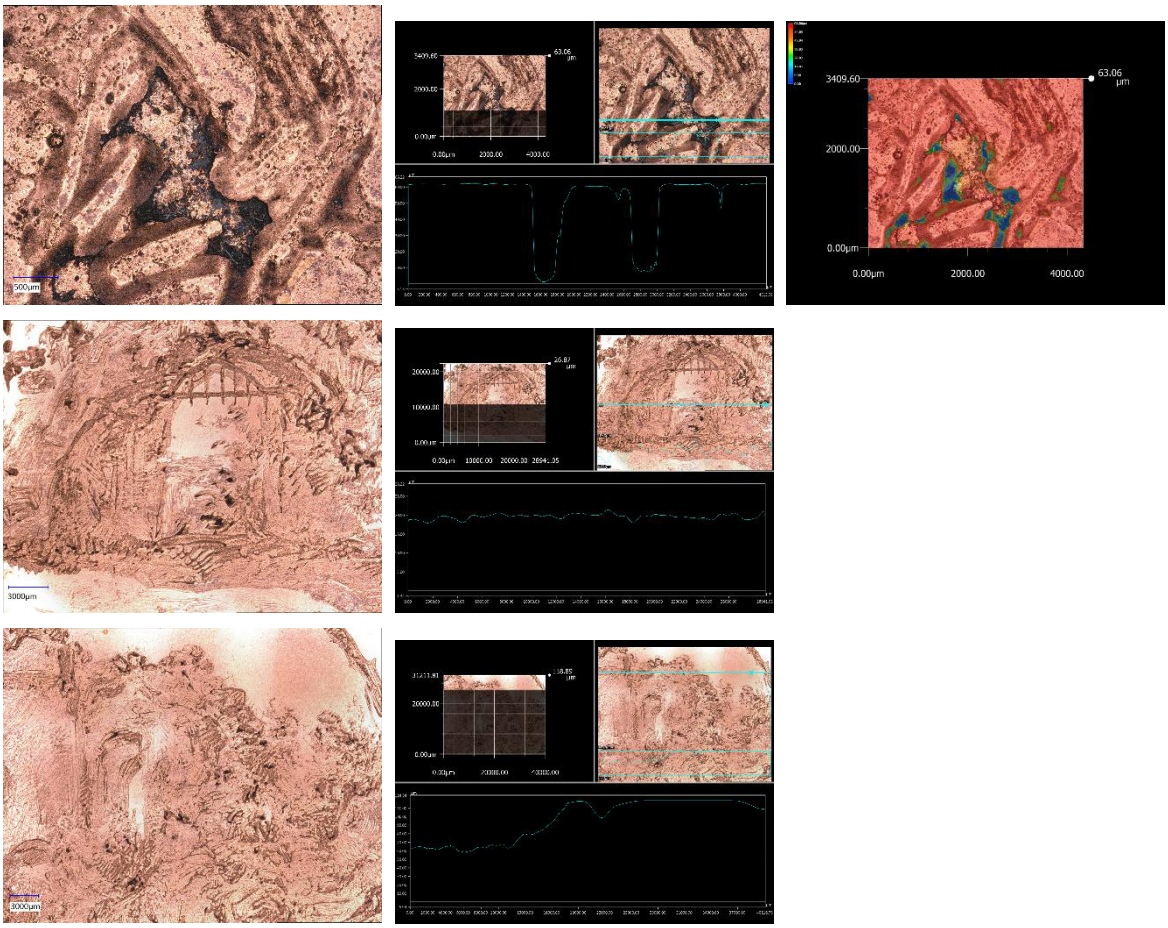
Digitalverweise:

REM, EDX REM, EDX (Zeiss EVO 60 XVP, Universität Wien)



Element	Atomic%	Element	Atomic%
C	59,54	C	57,82
O	16,52	O	26,22
Al	0,21	Al	0,2
Si	0,23	Si	0,63
S	1.74	S	1,82
Cl		Cl	0,23
K		K	0,21
Ca	0,22	Ca	0,75
Fe	0.11	Fe	0,47
Cu	23,28	Cu	7,83
Ag		Ag	3,82

Lichtmikroskopaufnahmen (z-Scans; Keyence, VHX-5000), Universität für Bodenkultur Wien



Inventarnr.: 83939/3 **Alte Inventarnr.:** MdA4, 221

Sammlungsgr.: 530 Metallbearbeitung

akt. Standort: Standorte-TMW/TMW-Museum/E5/3-102

Titel: Kupferdruckplatte

Hersteller_in: Theyer, Franz; Waidele, Erwin

Ort: Wien

Datierung: 1840 **bis** 1845

Maße:

Breite 14.5 cm

Tiefe 20 cm

Höhe 0.1 cm

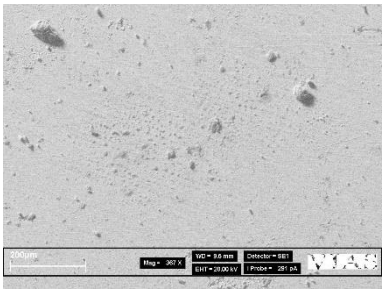
Beschreibung:

Befindet sich in Lade 4 (von oben gezählt) auf der mit schwarzem Stoff bespannten Tafel (dort befinden sich die Nummern 219-226, 228-235 und darunter 48).

Schlagworte: Kupfer

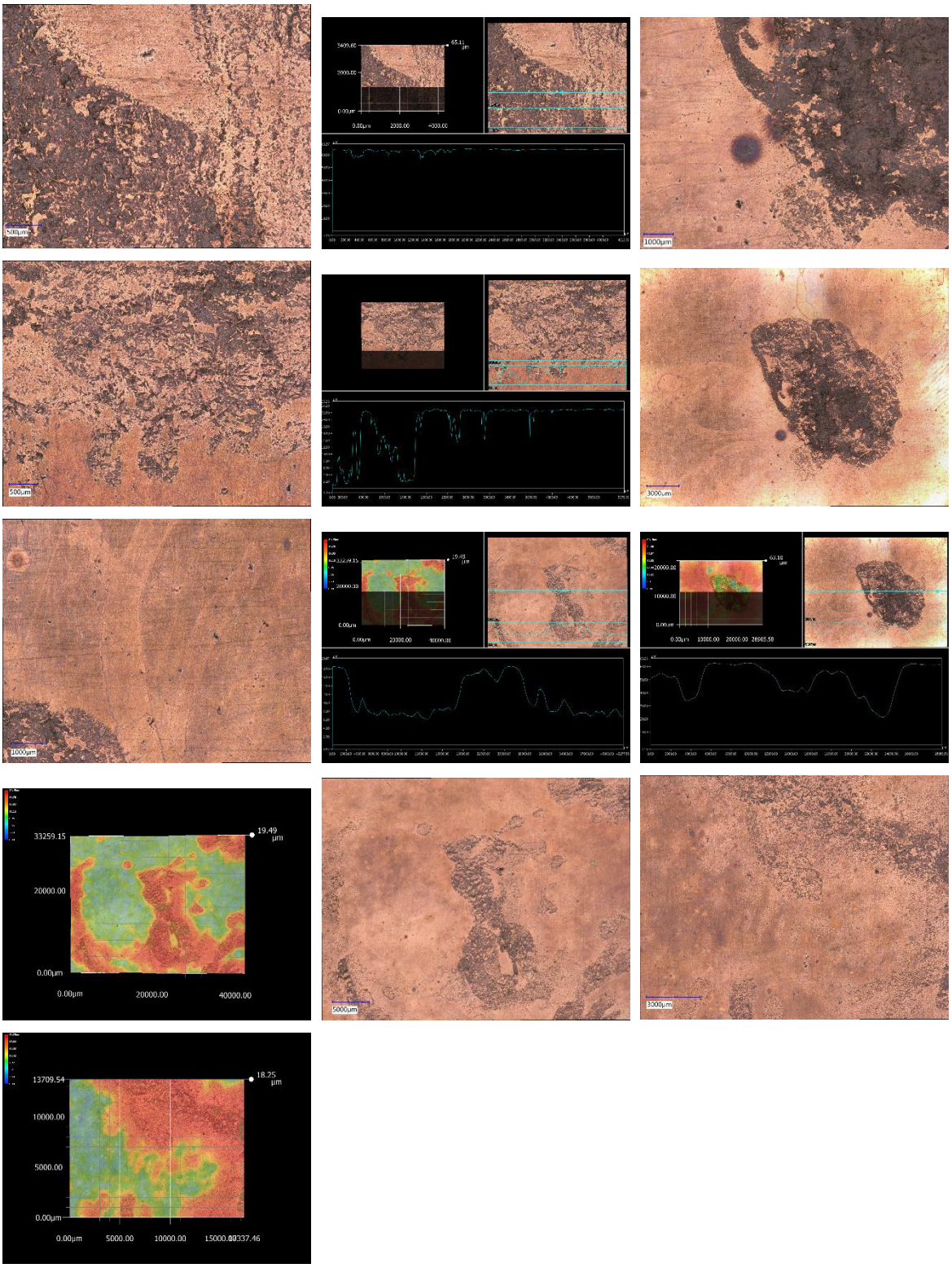
Digitalverweise:

REM, EDX (Zeiss EVO 60 XVP, Universität Wien)



Element	Atomic%	Element	Atomic%
C	60,44	C	51,76
O	14,87	O	34,24
Mg			0,29
Al		Al	0,56
Si		Si	4,16
S		S	0,28
Ca		Ca	5,86
Cu	24,69	Cu	2,85

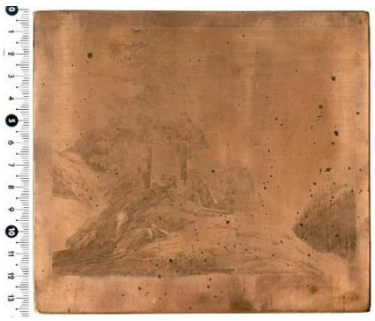
Lichtmikroskopaufnahmen (z-Scans; Keyence, VHX-5000), Universität für Bodenkultur Wien



Inventarnr.: 83939/4 **Alte Inventarnr.:** MdA4, 222

Sammlungsgr.: 530 Metallbearbeitung

akt. Standort: Standorte-TMW/TMW-Museum/E5/3-102



Titel: Kupferdruckplatte

Hersteller_in: Theyer, Franz; Waidele, Erwin

Ort: Wien

Datierung: 1840 **bis** 1845

Maße:

Breite 15.1 cm

Tiefe 13.5 cm

Höhe 0.1 cm

Beschreibung:

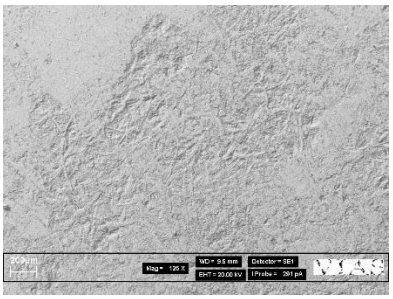
Befindet sich in Lade 4 (von oben gezählt) auf der mit schwarzem

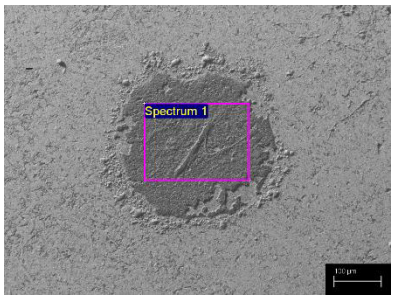
Stoff bespannten Tafel (dort befinden sich die Nummern 219-226, 228-235 und darunter 48).

Schlagworte: Kupfer

Digitalverweise:

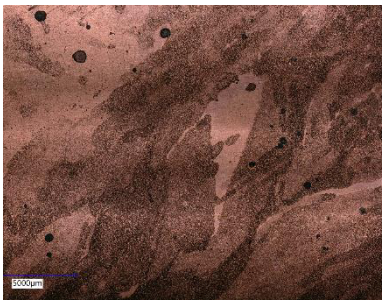
REM, EDX (Zeiss EVO 60 XVP, Universität Wien)

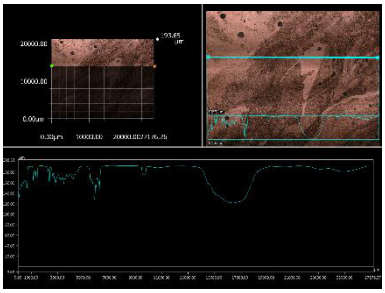


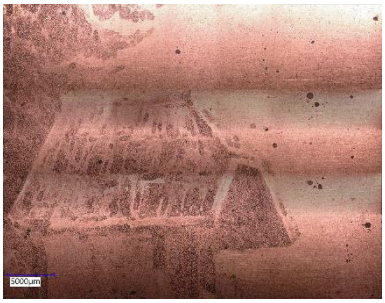


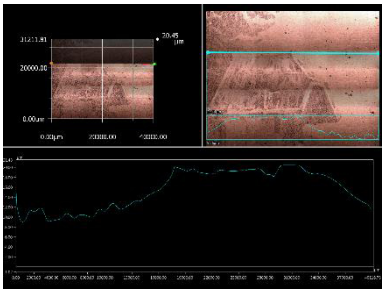
Element	Atomic%	Element	Atomic%
C K	64.67	C K	56.14
O K	17.96	O K	36.15
Si K	0.13	Na K	1.31
Cu K	17.24	Mg K	0.24
		Al K	0.26
		Si K	0.68
		S K	0.30
		K K	0.19
		Ca K	0.61
		Fe K	0.24
		Cu K	3.87

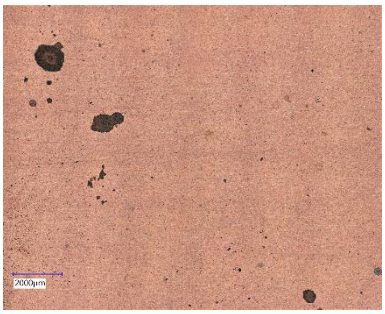
Lichtmikroskopaufnahmen (z-Scans; Keyence, VHX-5000), Universität für Bodenkultur Wien

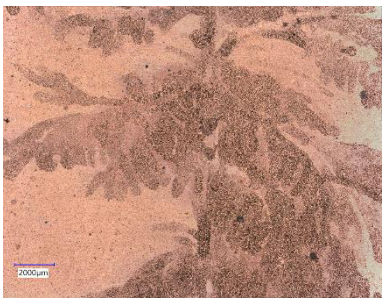


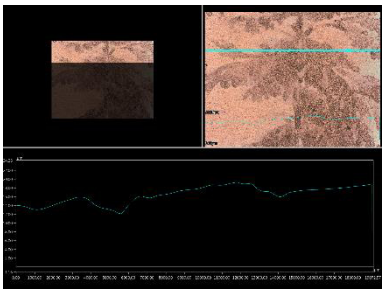


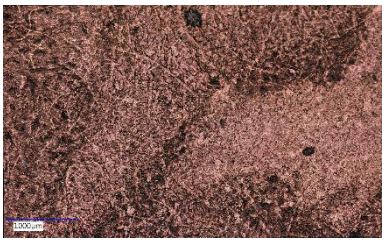








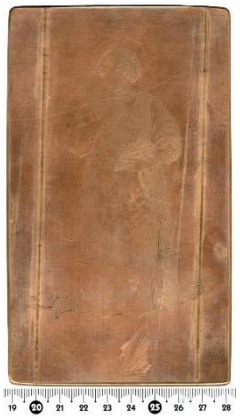




Inventarnr.: 83939/5 **Alte Inventarnr.:** MdA4, 223

Sammlungsgr.: 530 Metallbearbeitung

akt. Standort: Standorte-TMW/TMW-Museum/E5/3-102



Titel: Kupferdruckplatte

Hersteller_in: Theyer, Franz; Waidele, Erwin

Ort: Wien

Datierung: 1840 **bis** 1845

Maße:

Breite 9.4 cm

Tiefe 16 cm

Höhe 0.1 cm

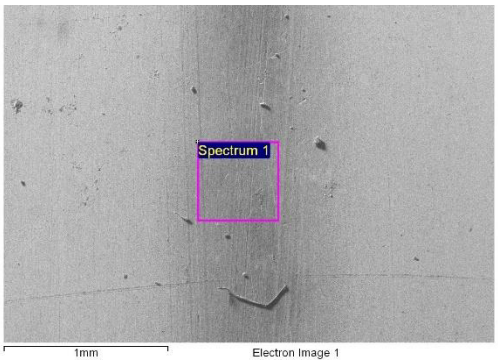
Beschreibung:

Befindet sich in Lade 4 (von oben gezählt) auf der mit schwarzem Stoff bespannten Tafel (dort befinden sich die Nummern 219-226, 228-235 und darunter 48).

Schlagworte: Kupfer

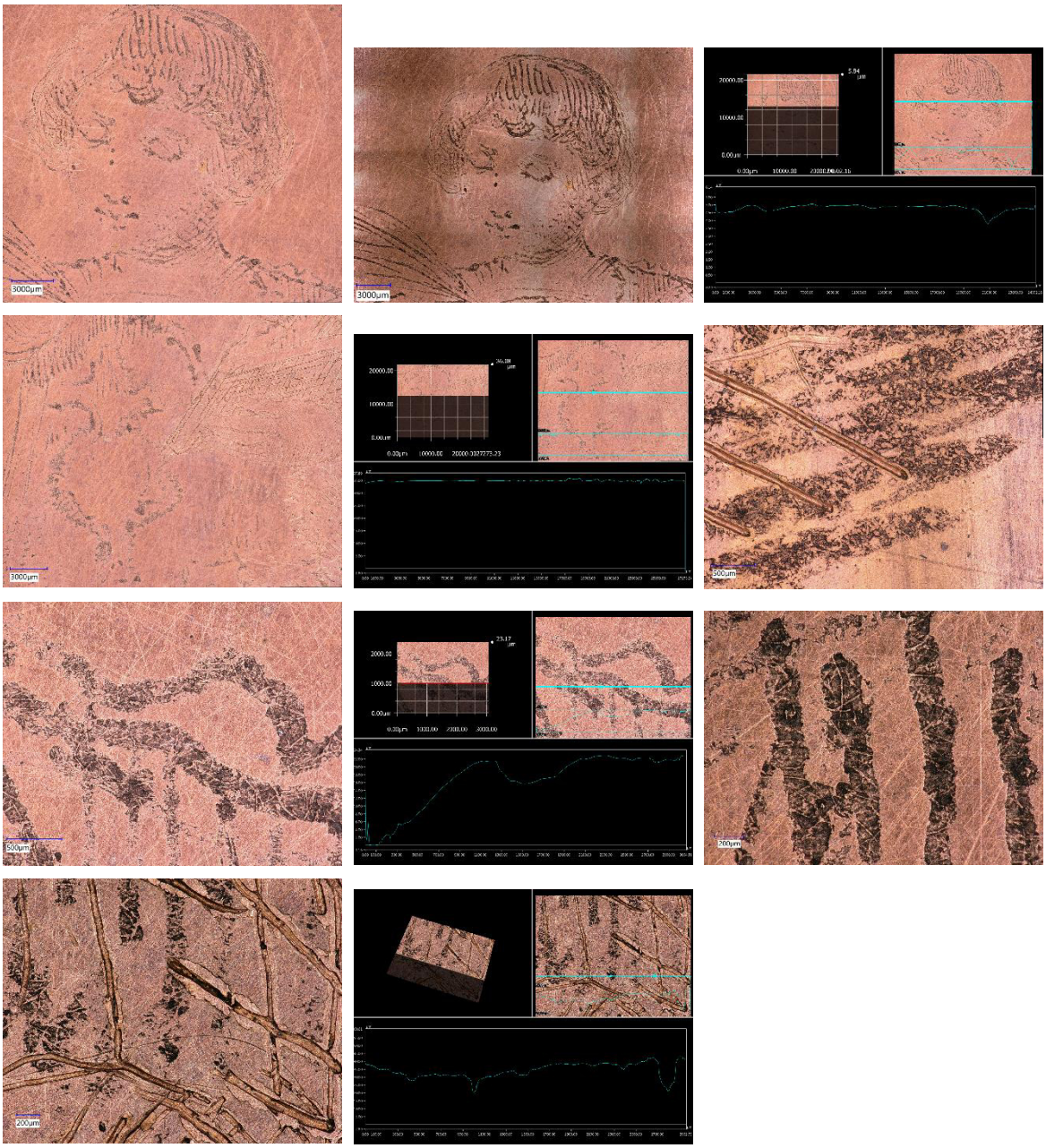
Digitalverweise:

REM, EDX (Zeiss Supra 55 VP, Universität Wien)



Element	Atomic%
C	67,31
O	18,67
S	0.41
Cu	13,62

Lichtmikroskopaufnahmen (z-Scans; Keyence, VHX-5000), Universität für Bodenkultur Wien



Inventarnr.: 83939/6 **Alte Inventarnr.:** MdA4, 224

Sammlungsgr.: 530 Metallbearbeitung

akt. Standort: Standorte-TMW/TMW-Museum/E5/3-102

Titel: Kupferdruckplatte

Hersteller_in: Theyer, Franz; Waidele, Erwin

Ort: Wien

Datierung: 1840 **bis** 1845

Maße:

Breite 10 cm

Tiefe 7.5 cm

Höhe 0.1 cm

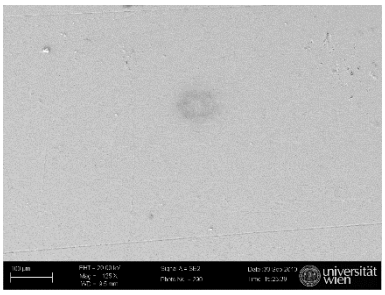
Beschreibung:

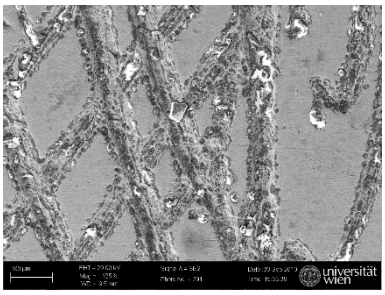
Befindet sich in Lade 4 (von oben gezählt) auf der mit schwarzem Stoff bespannten Tafel (dort befinden sich die Nummern 219-226, 228-235 und darunter 48).

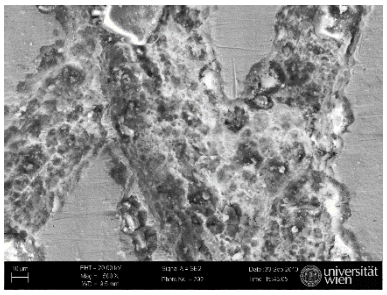
Schlagworte: Kupfer, versilbert

Digitalverweise:

REM, EDX (Zeiss Supra 55 VP, Universität Wien)

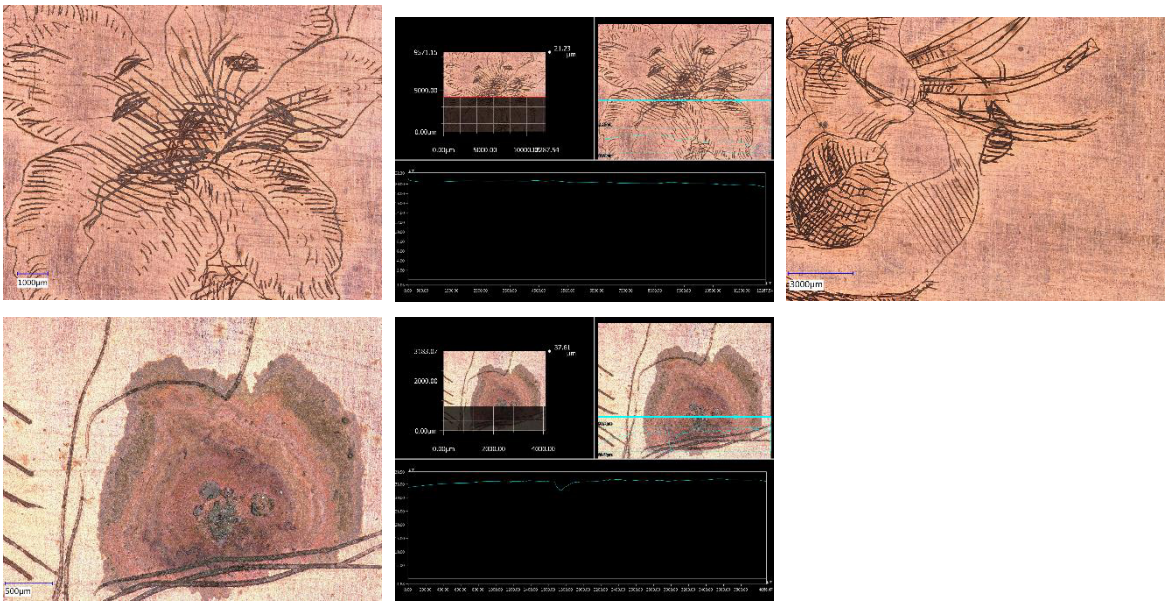






Element	Atomic%	Element	Atomic%
C	57,12	C	56,59
O	32,16	O	13,02
Mg	0,37	Cu	30,39
Si	0,47		
S	0,44		
Ca	0,72		
Fe	0,39		
Cu	7,26		
Ag	1,06		

Lichtmikroskopaufnahmen (z-Scans; Keyence, VHX-5000, Universität für Bodenkultur Wien)



Inventarnr.: 83939/7 **Alte Inventarnr.:** MdA4, 225

Sammlungsgr.: 530 Metallbearbeitung

akt. Standort: Standorte-TMW/TMW-Museum/E5/3-102

Titel: Kupferdruckplatte

Hersteller_in: Theyer, Franz; Waidele, Erwin

Ort: Wien

Datierung: 1840 **bis** 1845

Maße:

Breite 10.6 cm

Tiefe 14 cm

Höhe 0.1 cm

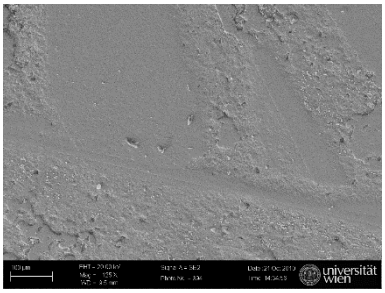
Beschreibung:

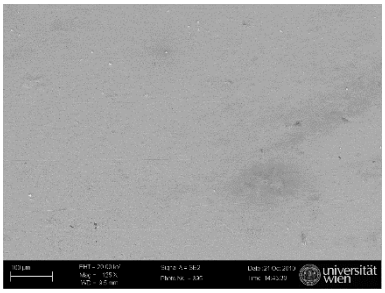
Befindet sich in Lade 4 (von oben gezählt) auf der mit schwarzem Stoff bespannten Tafel (dort befinden sich die Nummern 219-226, 228-235 und darunter 48).

Schlagworte: Kupfer, versilbert

Digitalverweise:

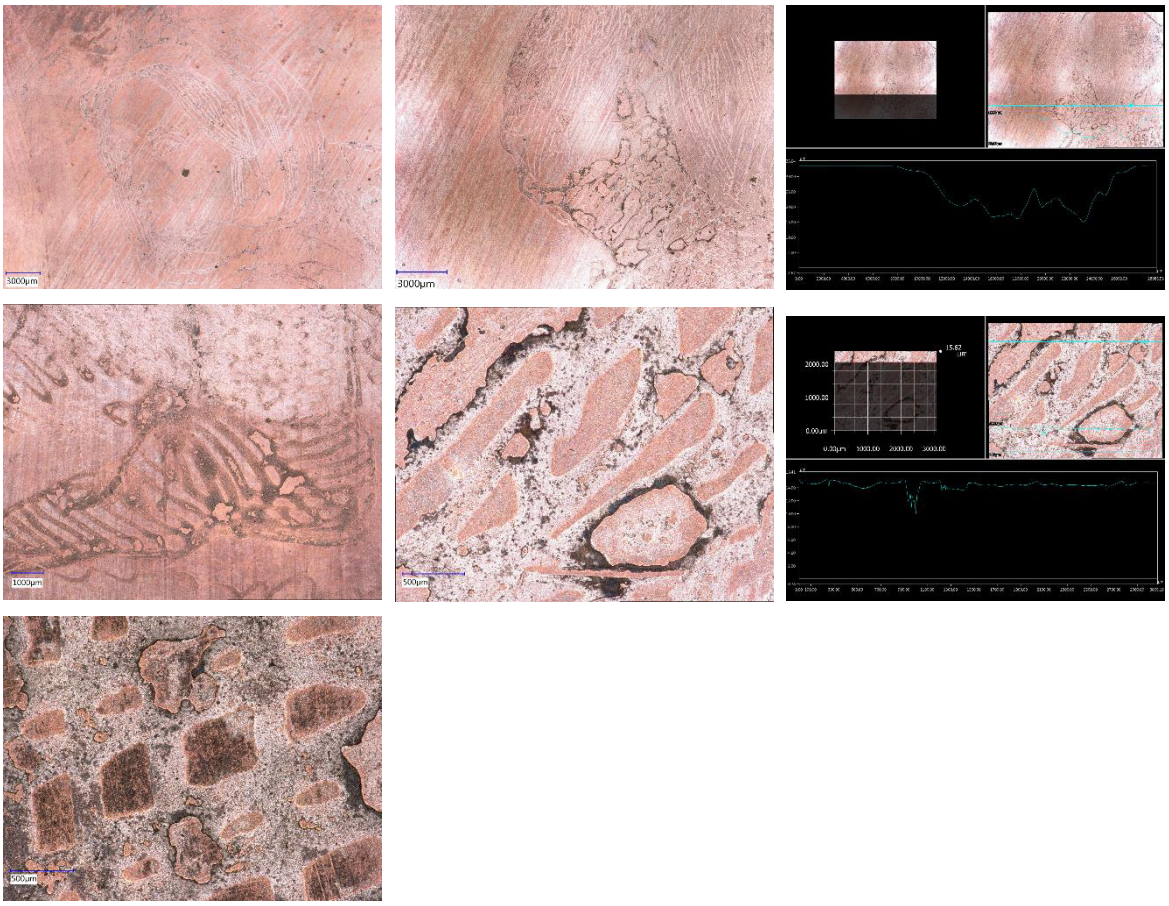
REM, EDX (Zeiss Supra 55 VP, Universität Wien)





Element	Atomic%	Element	Atomic%
C	44,74	C	44,62
O	16,43	O	17,35
S	0,3	Cu	38,03
Cu	34,41		
Ag	4,12		

Lichtmikroskopaufnahmen (z-Scans; Keyence, VHX-5000), Universität für Bodenkultur Wien



Lichtmikroskopaufnahmen (Olympus GX51, Happy Platting GmbH, Wiener Neustadt)

Druck auf Papier (TMW Archiv)

Inventarnr.: 83939/8 **Alte Inventarnr.:** MdA4, 226

Sammlungsgr.: 530 Metallbearbeitung

akt. Standort: Standorte-TMW/TMW-Museum/E5/3-102

Titel: Kupferdruckplatte

Hersteller_in: Theyer, Franz; Waidele, Erwin

Ort: Wien

Datierung: 1840 **bis** 1845

Maße:

Breite 10.5 cm

Tiefe 13.8 cm

Höhe 0.1 cm

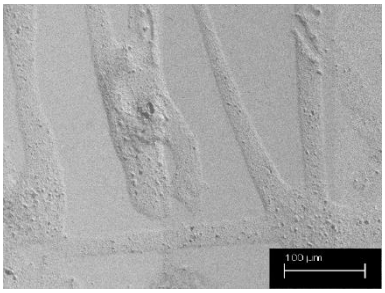
Beschreibung:

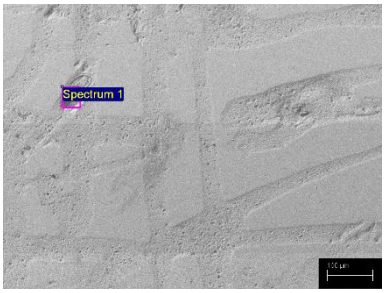
Befindet sich in Lade 4 (von oben gezählt) auf der mit schwarzem Stoff bespannten Tafel (dort befinden sich die Nummern 219-226, 228-235 und darunter 48).

Schlagworte: Kupfer

Digitalverweise:

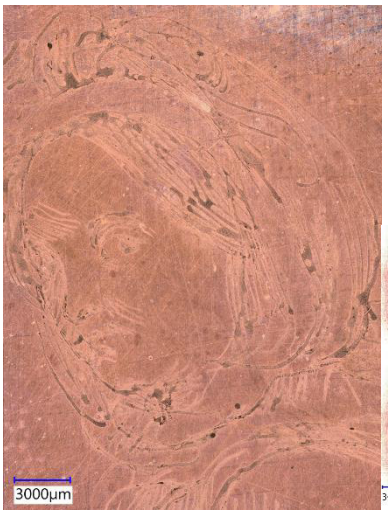
REM, EDX (Zeiss EVO 60 XVP, Universität Wien)

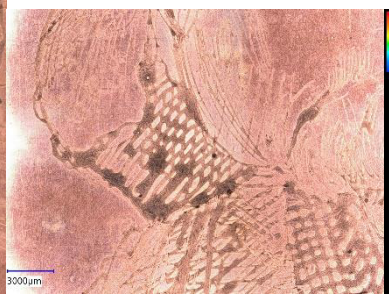


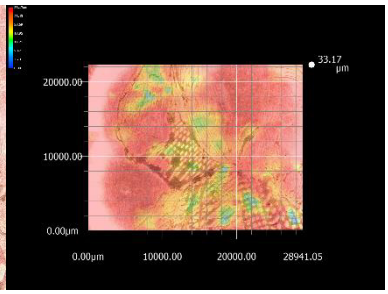


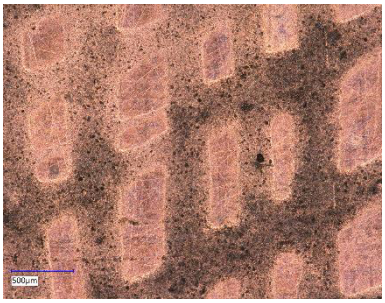
Element	Atomic%	Element	Atomic%
C K	54.33	C K	74.37
O K	12.01	O K	17.09
Cu K	33.65	Al K	0.10
		Si K	0.38
		S K	0.26
		K K	0.22
		Ca K	0.24
		Fe K	0.14
		Cu K	7.19
		Cu K	3.87

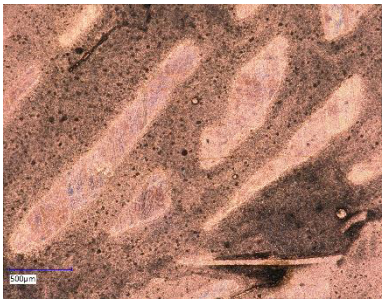
Lichtmikroskopaufnahmen (z-Scans; Keyence, VHX-5000), Universität für Bodenkultur Wien

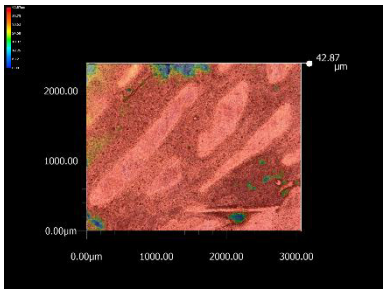


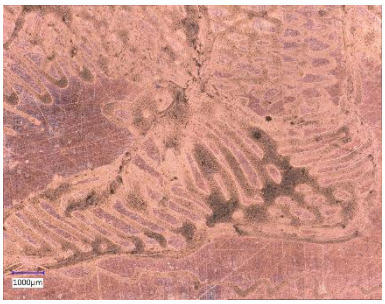


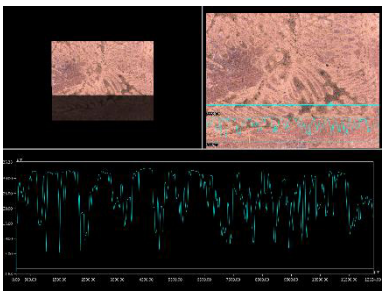












Druck auf Papier (TMW Archiv)

Inventarnr.: 83939/9 **Alte Inventarnr.:** MdA4, 228

Sammlungsgr.: 530 Metallbearbeitung

akt. Standort: Standorte-TMW/TMW-Museum/E5/3-102

Titel: Kupferdruckplatte

Hersteller_in: Theyer, Franz; Waidele, Erwin

Ort: Wien

Datierung: 1840 **bis** 1845

Maße:

Breite 6.9 cm

Tiefe 10 cm

Höhe 0.1 cm

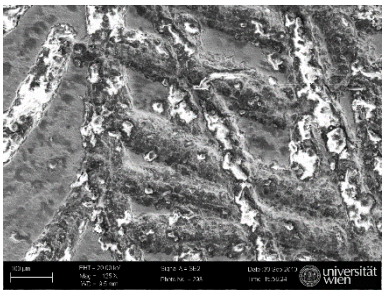
Beschreibung:

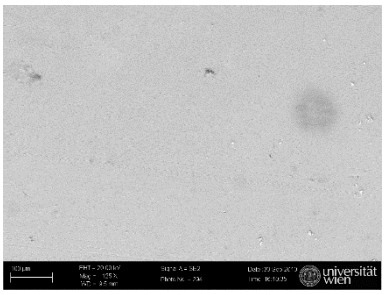
Befindet sich in Lade 4 (von oben gezählt) auf der mit schwarzem Stoff bespannten Tafel (dort befinden sich die Nummern 219-226, 228-235 und darunter 48).

Schlagworte: Kupfer, versilbert

Digitalverweise:

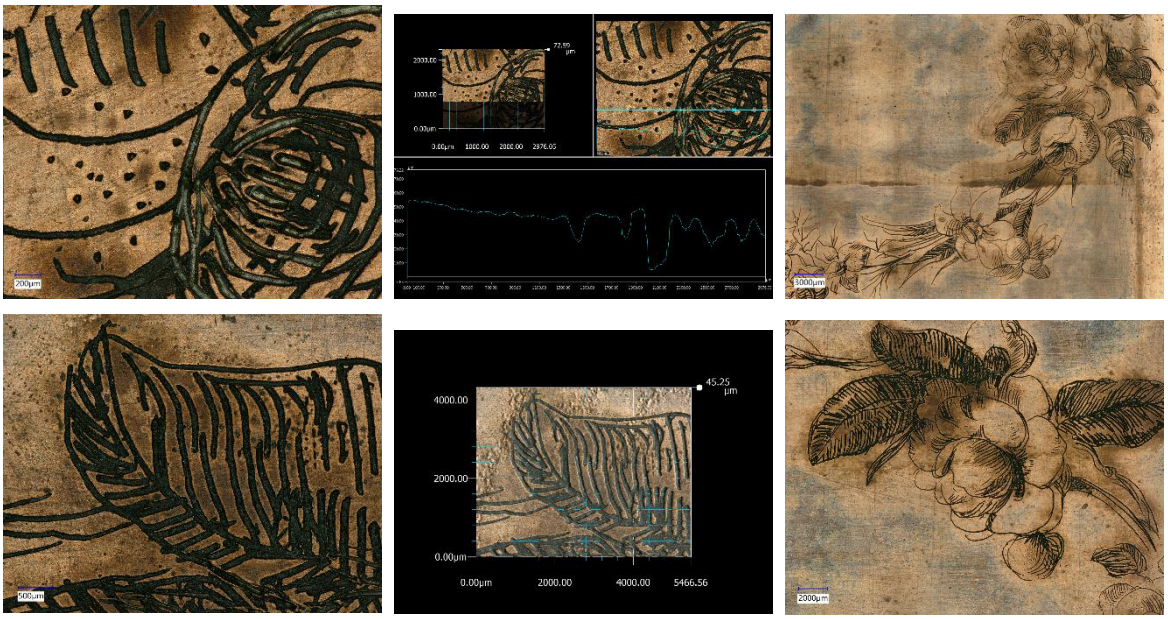
REM, EDX (Zeiss Supra 55 VP, Universität Wien)





Element	Atomic%	Element	Atomic%	Element	Atomic%
C	54,97	C	61,49	C K	50,34
O	35,48	O	11,69	O K	10,75
Si	0,63	Cu	26,27	Cu	38,9
S	0,44	Ag	0,55		
Ca	0,89				
Cu	6,96				
Ag	0,64				

Lichtmikroskopaufnahmen (z-Scans; Keyence, VHX-5000), Universität für Bodenkultur Wien



Inventarnr.: 83939/10 **Alte Inventarnr.:** MdA4, 229

Sammlungsgr.: 530 Metallbearbeitung

akt. Standort: Standorte-TMW/TMW-Museum/E5/3-102

Titel: Kupferdruckplatte

Hersteller_in: Theyer, Franz; Waidele, Erwin

Ort: Wien

Datierung: 1840 **bis** 1845

Maße:

Breite 10.5 cm

Tiefe 15.8 cm

Höhe 0.1 cm

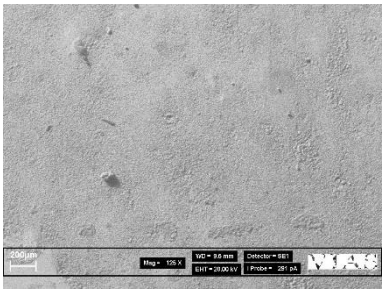
Beschreibung:

Befindet sich in Lade 4 (von oben gezählt) auf der mit schwarzem Stoff bespannten Tafel (dort befinden sich die Nummern 219-226, 228-235 und darunter 48).

Schlagworte: Kupfer, versilbert

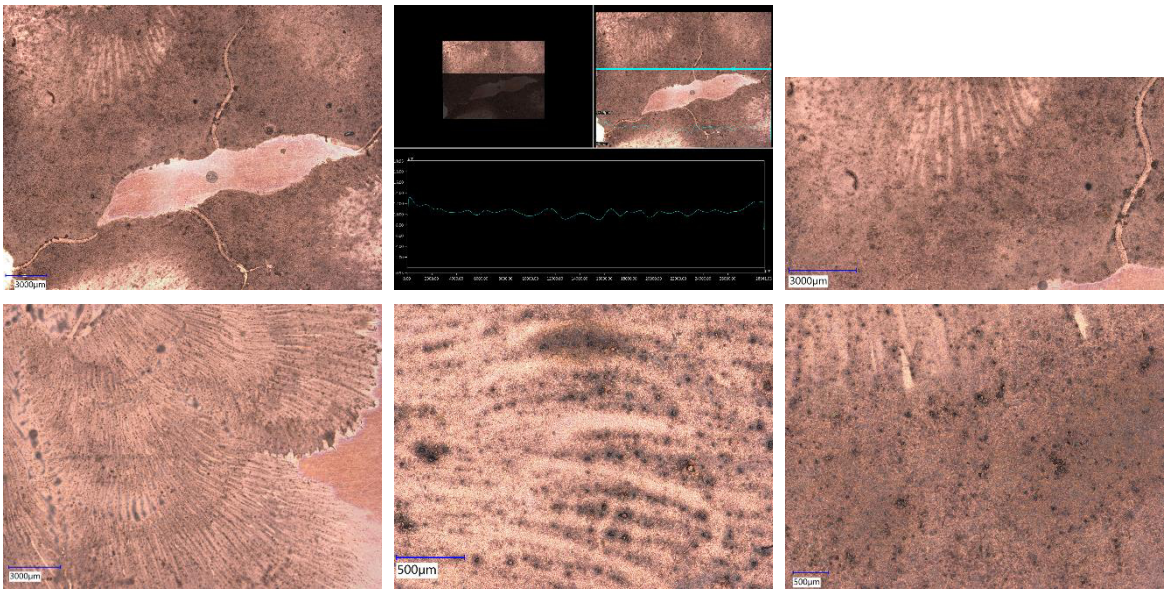
Digitalverweise:

REM, EDX (Zeiss EVO 60 XVP, Universität Wien)



Element	Atomic%	Element	Atomic%
C	67,48	C	55,39
O	19,2	O	33,67
Mg		Mg	0,32
Al		Al	0,18
Si	0,15	Si	0,46
S	0,17	S	0,39
Cl	0,07	Cl	0,21
K	0,1	K	0,41
Ca	0,3	Ca	0,83
Cu	11,88	Cu	7,73
Ag	0,65	Ag	0,4

Lichtmikroskopaufnahmen (z-Scans; Keyence, VHX-5000), Universität für Bodenkultur Wien



Inventarnr.: 83939/11 **Alte Inventarnr.:** MdA4, 230

Sammlungsgr.: 530 Metallbearbeitung

akt. Standort: Standorte-TMW/TMW-Museum/E5/3-102

Titel: Kupferdruckplatte

Hersteller_in: Theyer, Franz; Waidele, Erwin

Ort: Wien

Datierung: 1840 **bis** 1845

Maße:

Breite 12.5 cm

Tiefe 14.5 cm

Höhe 0.1 cm

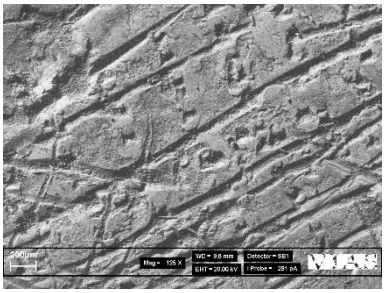
Beschreibung:

Befindet sich in Lade 4 (von oben gezählt) auf der mit schwarzem Stoff bespannten Tafel (dort befinden sich die Nummern 219-226, 228-235 und darunter 48).

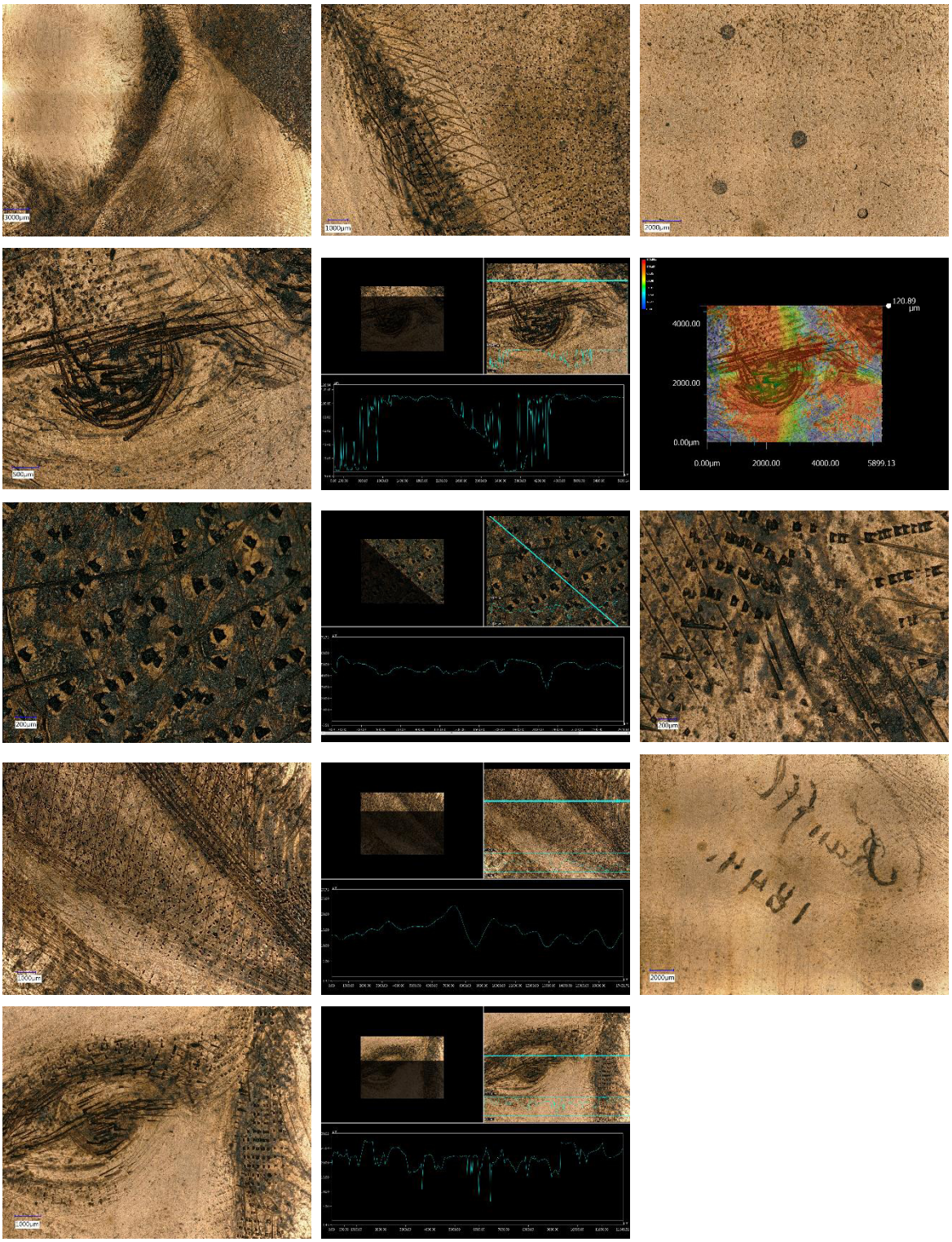
Schlagworte: Kupfer

Digitalverweise:

REM (Zeiss EVO 60 XVP, Universität Wien)



Lichtmikroskopaufnahmen (z-Scans; Keyence, VHX-5000), Universität für Bodenkultur Wien



Inventarnr.: 83939/12 **Alte Inventarnr.:** MdA4, 231

Sammlungsgr.: 530 Metallbearbeitung

akt. Standort: Standorte-TMW/TMW-Museum/E5/3-102

Titel: Kupferdruckplatte

Hersteller_in: Theyer, Franz; Waidele, Erwin

Ort: Wien

Datierung: 1840 **bis** 1845

Maße:

Breite 6.5 cm

Tiefe 10.3 cm

Höhe 0.1 cm

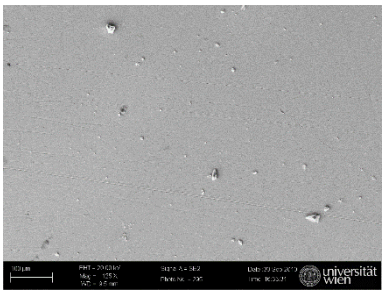
Beschreibung:

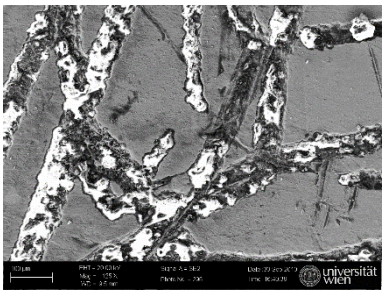
Befindet sich in Lade 4 (von oben gezählt) auf der mit schwarzem Stoff bespannten Tafel (dort befinden sich die Nummern 219-226, 228-235 und darunter 48).

Schlagworte: Kupfer

Digitalverweise:

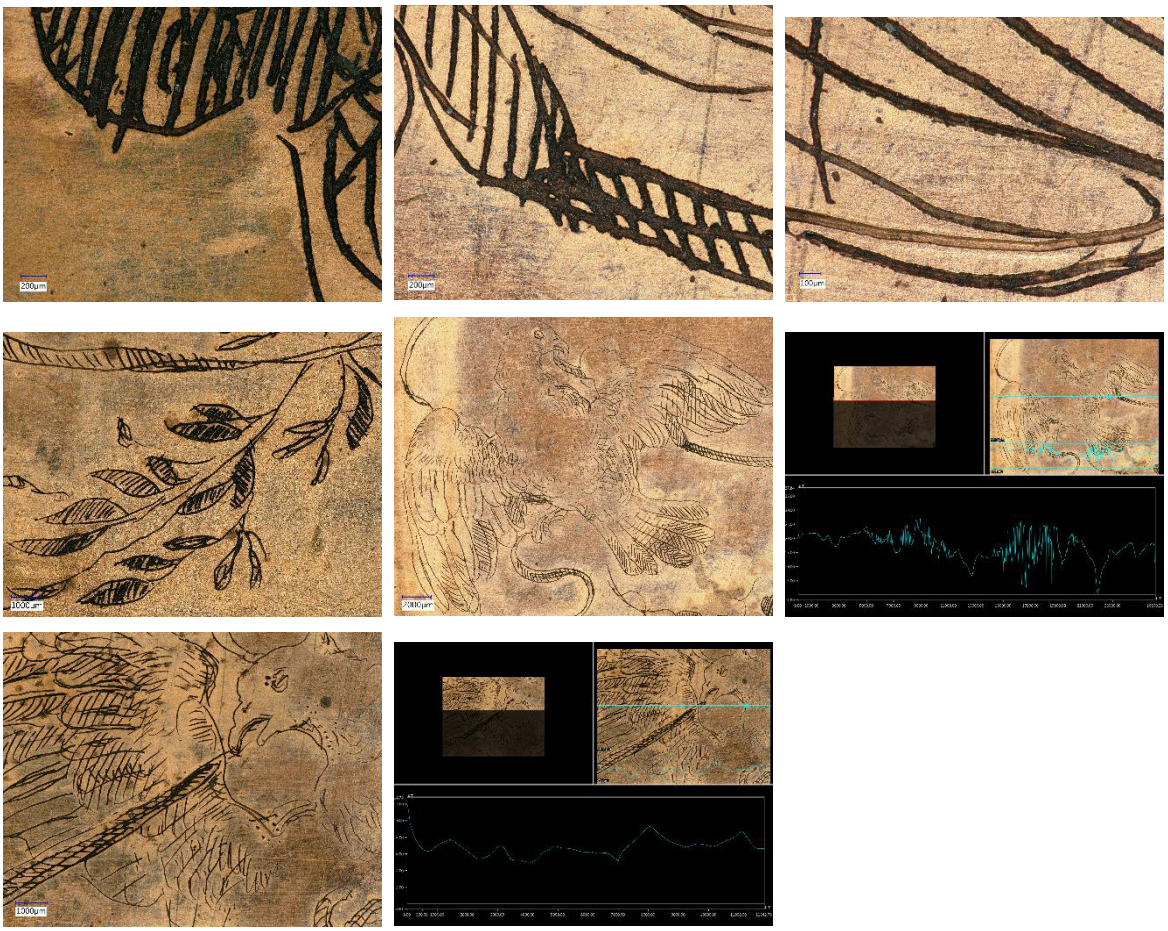
REM, EDX (Zeiss Supra 55 VP, Universität Wien)





Element	Atomic%
C	59,88
O	33,93
Si	0,82
S	0,55
Ca	0,89
Cu	3,94

Lichtmikroskopaufnahmen (z-Scans; Keyence, VHX-5000), Universität für Bodenkultur Wien



Inventarnr.: 83939/13 **Alte Inventarnr.:** MdA4, 232

Sammlungsgr.: 530 Metallbearbeitung

akt. Standort: Standorte-TMW/TMW-Museum/E5/3-102

Titel: Kupferdruckplatte

Hersteller_in: Theyer, Franz

Ort: Wien

Datierung: 1840 **bis** 1845

Maße:

Breite 17 cm

Tiefe 14.2 cm

Höhe 0.1 cm

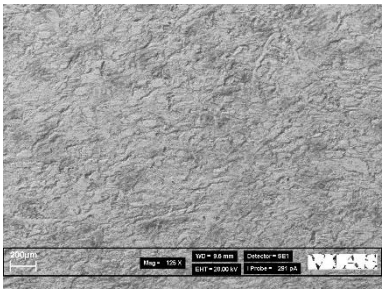
Beschreibung:

Befindet sich in Lade 4 (von oben gezählt) auf der mit schwarzem Stoff bespannten Tafel (dort befinden sich die Nummern 219-226, 228-235 und darunter 48).

Schlagworte: Kupfer

Digitalverweise:

REM, EDX (Zeiss EVO 60 XVP, Universität Wien)



Element	Atomic%
C	62,55
O	20,15
Si	0,2
S	0,21
Ca	0,1
Cu	16,8

Lichtmikroskopaufnahmen (z-Scans; Keyence, VHX-5000), Universität für Bodenkultur Wien

Inventarnr.: 83939/14 **Alte Inventarnr.:** MdA4, 233

Sammlungsgr.: 530 Metallbearbeitung

akt. Standort: Standorte-TMW/TMW-Museum/E5/3-102

Titel: Kupferdruckplatte

Hersteller_in: Theyer, Franz; Waidele, Erwin

Ort: Wien

Datierung: 1840 **bis** 1845

Maße:

Breite 12.7 cm

Tiefe 17 cm

Höhe 0.1 cm

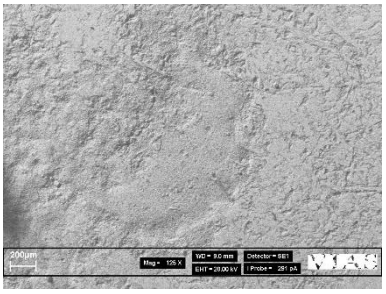
Beschreibung:

Befindet sich in Lade 4 (von oben gezählt) auf der mit schwarzem Stoff bespannten Tafel (dort befinden sich die Nummern 219-226, 228-235 und darunter 48).

Schlagworte: Kupfer

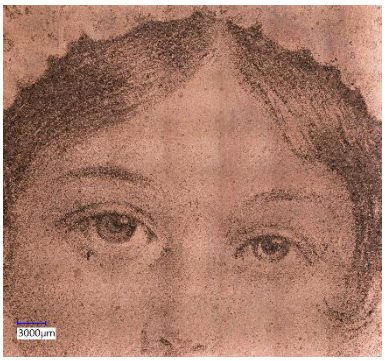
Digitalverweise:

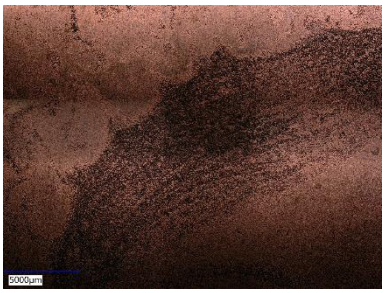
REM, EDX (Zeiss EVO 60 XVP, Universität Wien)

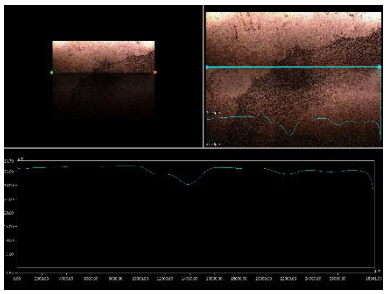


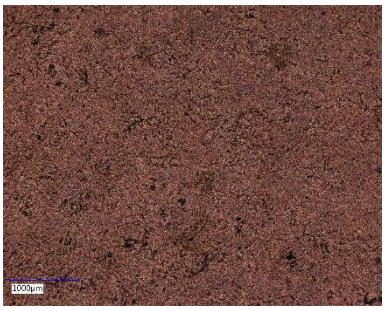
Element	Atomic%
C	64,15
O	18,87
Si	0,31
S	0,13
Ca	0,12
Cu	16,42

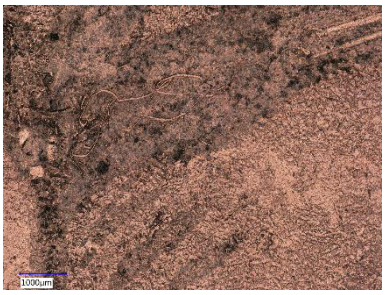
Lichtmikroskopaufnahmen (z-Scans; Keyence, VHX-5000), Universität für Bodenkultur Wien

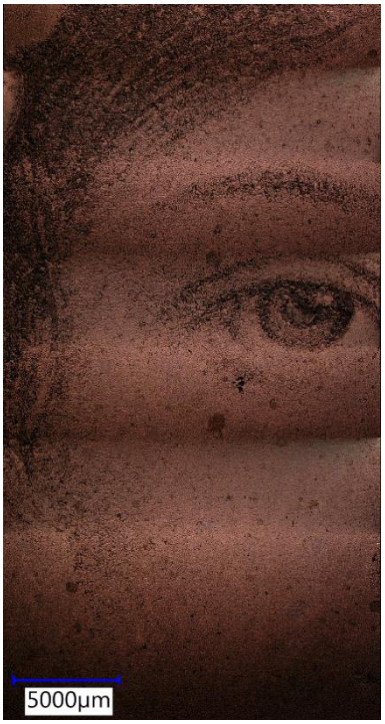


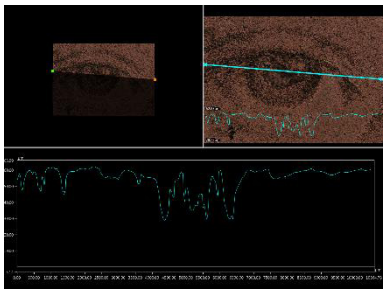


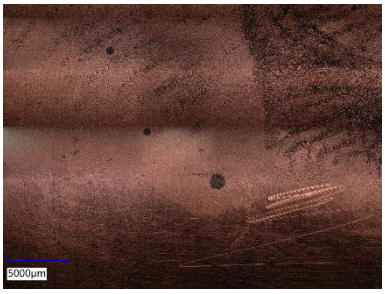


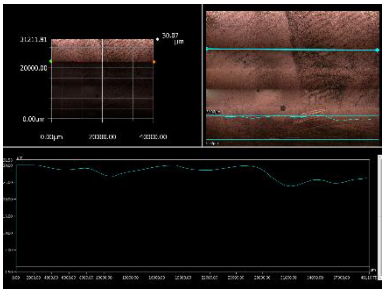












Inventarnr.: 83939/15 **Alte Inventarnr.:** MdA4, 234

Sammlungsgr.: 530 Metallbearbeitung

akt. Standort: Standorte-TMW/TMW-Museum/E5/3-102

Titel: Kupferdruckplatte

Hersteller_in: Theyer, Franz; Waidele, Erwin

Ort: Wien

Datierung: 1840 **bis** 1845

Maße:

Breite 14.4 cm

Tiefe 12.8 cm

Höhe 0.1 cm

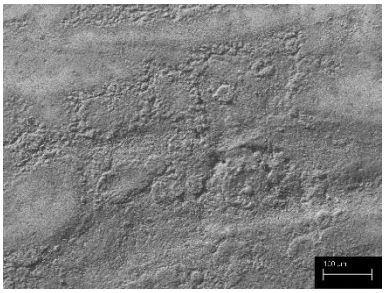
Beschreibung:

Befindet sich in Lade 4 (von oben gezählt) auf der mit schwarzem Stoff bespannten Tafel (dort befinden sich die Nummern 219-226, 228-235 und darunter 48).

Schlagworte: Kupfer, versilbert

Digitalverweise:

REM, EDX (Zeiss EVO 60 XVP, Universität Wien)



Element	Atomic%	Element	Atomic%
C K	45.80	C K	57.58
O K	42.39	O K	32.97
Na K	3.02	Al K	0.17
Si K	0.36	Si K	0.46
S K	1.22	S K	0.66
K K	0.20	K K	0.17
Ca K	0.36	Ca K	0.58
Cu K	5.83	Fe K	0.17
Ag L	0.83	Cu K	6.84
		Ag L	0.40

Lichtmikroskopaufnahmen (z-Scans; Keyence, VHX-5000), Universität für Bodenkultur Wien

Druck auf Papier (TMW Archiv)

Inventarnr.: 83939/16 **Alte Inventarnr.:** MdA4, 235

Sammlungsgr.: 530 Metallbearbeitung

akt. Standort: Standorte-TMW/TMW-Museum/E5/3-102

Titel: Kupferdruckplatte

Hersteller_in: Theyer, Franz; Waidele, Erwin

Ort: Wien

Datierung: 1840 **bis** 1845

Maße:

Breite 8.4 cm

Tiefe 13.3 cm

Höhe 0.1 cm

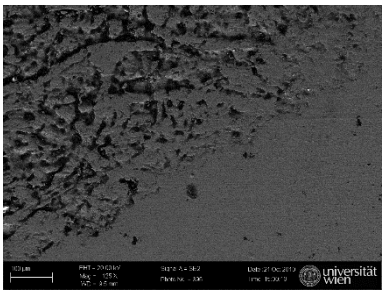
Beschreibung:

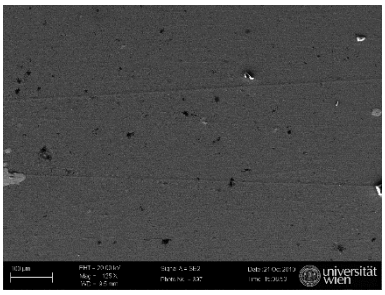
Befindet sich in Lade 4 (von oben gezählt) auf der mit schwarzem Stoff bespannten Tafel (dort befinden sich die Nummern 219-226, 228-235 und darunter 48).

Schlagworte: Kupfer

Digitalverweise:

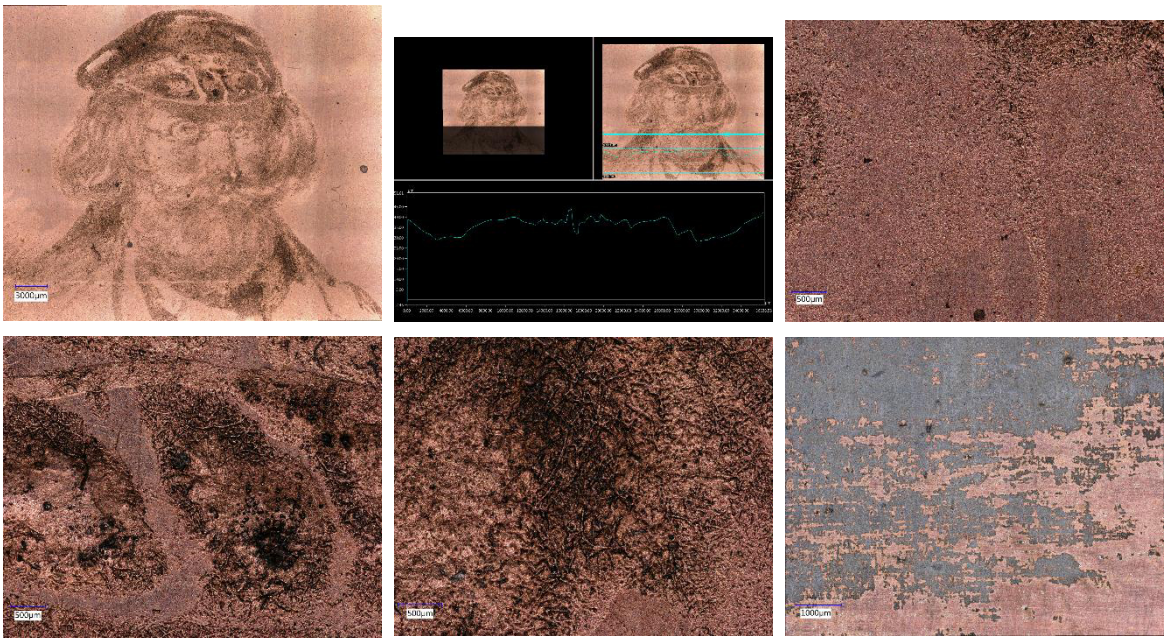
REM, EDX (Zeiss Supra 55 VP, Universität Wien)





Element	Atomic%	Element	Atomic%
C	62,38	C	49,98
O	20,09	O	11,93
Ca	0,32		
Cu	17,21	Cu	38,09

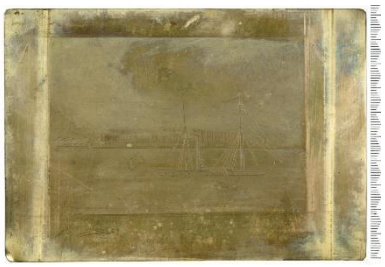
Lichtmikroskopaufnahmen (z-Scans; Keyence, VHX-5000), Universität für Bodenkultur Wien



Inventarnr.: 83939/17 **Alte Inventarnr.:** MdA4, 236

Sammlungsgr.: 530 Metallbearbeitung

akt. Standort: Standorte-TMW/TMW-Museum/E5/3-102



Titel: Kupferdruckplatte

Hersteller_in: Theyer, Franz; Waidele, Erwin

Ort: Wien

Datierung: 1840 **bis** 1845

Maße:

Breite 14.8 cm

Tiefe 10.4 cm

Höhe 0.1 cm

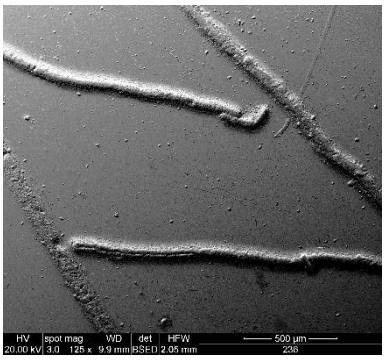
Beschreibung:

Befindet sich in Lade 3 (von oben gezählt) auf der mit schwarzem Stoff bespannten Tafel (dort befinden sich die Nummern 236-253).

Schlagworte: Kupfer, versilbert

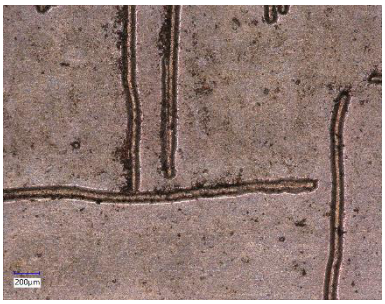
Digitalverweise:

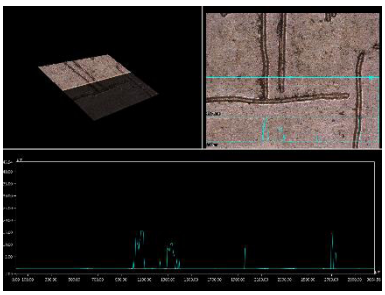
REM, EDX (Zeiss, Universität für angewandte Kunst Wien)

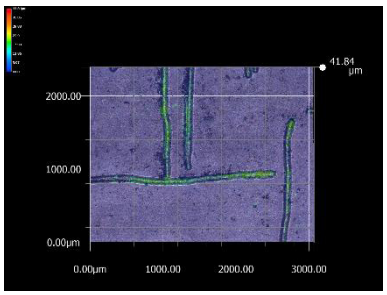


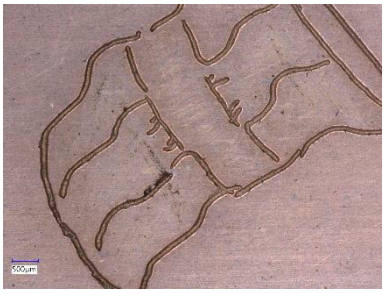
Element	Atomic%	Element	Atomic%
C	4,20	C	6,37
O	5,17	O	3,78
Cu	51,39	Cu	12,77
Ag	39,24	Ag	77,08

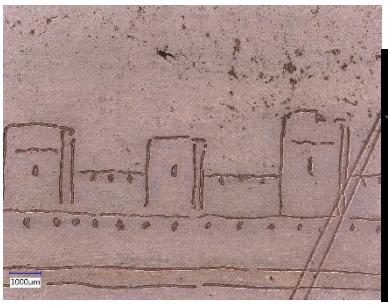
Lichtmikroskopaufnahmen (z-Scans; Keyence, VHX-5000), Universität für Bodenkultur Wien

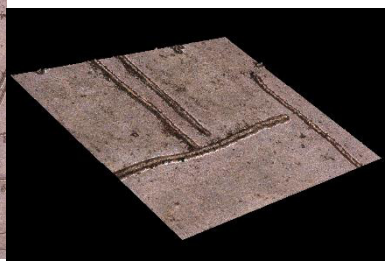


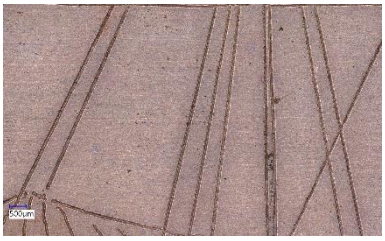






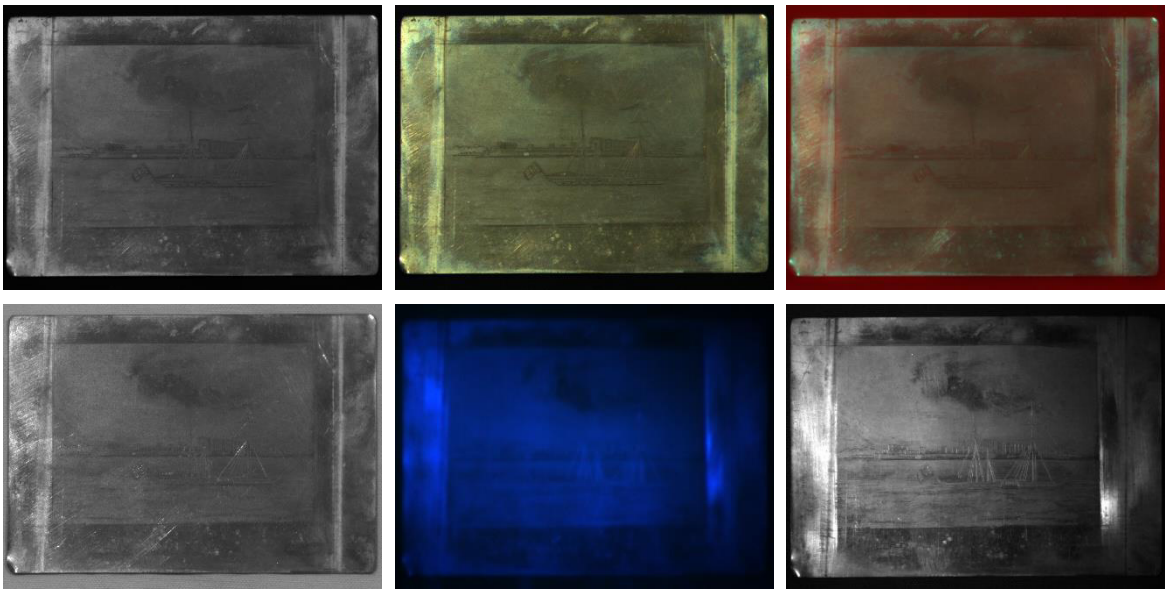






Lichtmikroskopaufnahmen Happy Platting, Wiener Neustadt

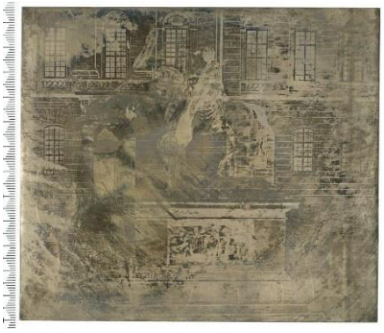
Multispektralkamera, Rumänien



Inventarnr.: 83939/18 **Alte Inventarnr.:** MdA4, 237

Sammlungsgr.: 5 Handwerkliche und industrielle Produktion

akt. Standort: Standorte-TMW/TMW-Museum/E5/3-102



Titel: Kupferdruckplatte, geätzte Daguerreotypie

Hersteller_in: Natterer, Johann, Natterer, Joseph, Berres, Joseph

Ort: Wien

Datierung: 1840 **bis** 1845

Maße:

Breite 14.4 cm

Tiefe 12.7 cm

Höhe 0.1 cm

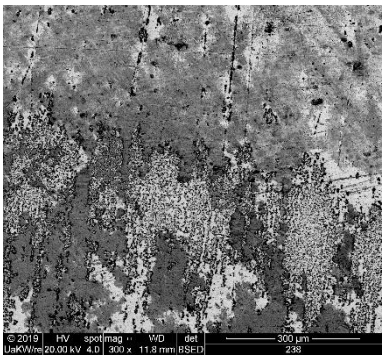
Beschreibung:

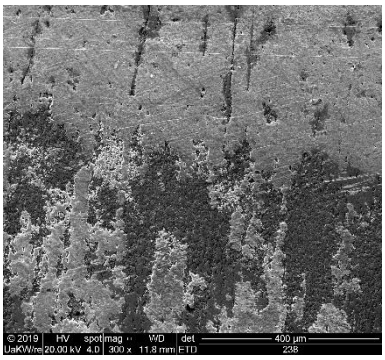
Befindet sich in Lade 3 (von oben gezählt) auf der mit schwarzem Stoff bespannten Tafel (dort befinden sich die Nummern 236-253).

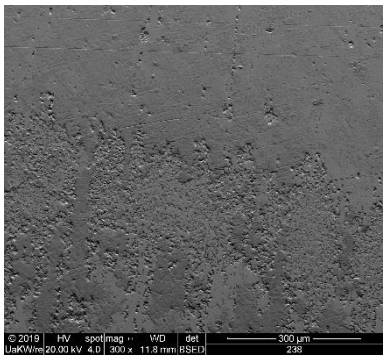
Schlagworte: Kupfer, versilbert

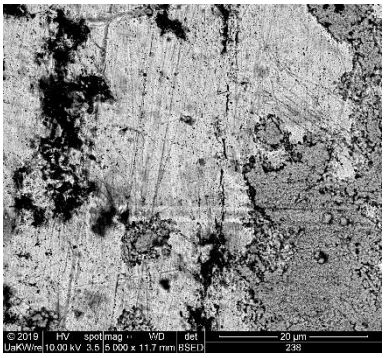
Digitalverweise:

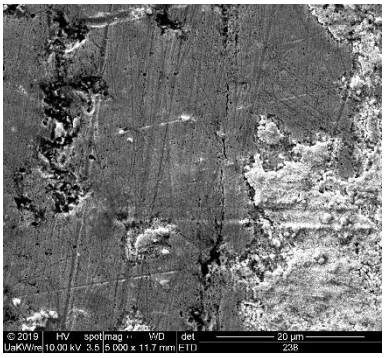
REM, EDX (Zeiss, Universität für angewandte Kunst Wien)

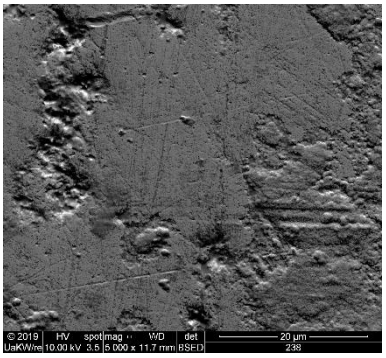


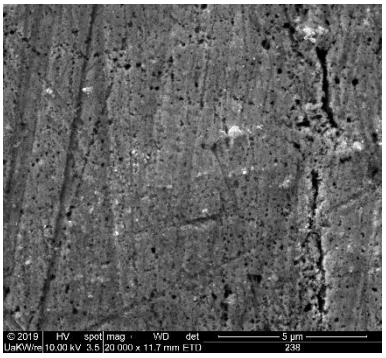


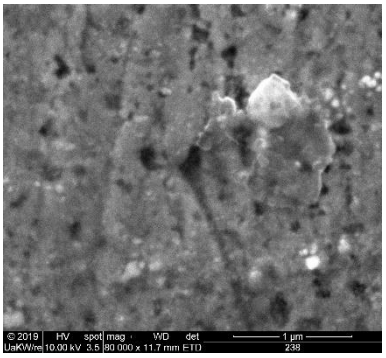


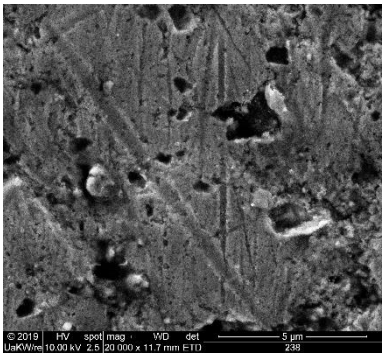

© 2019 HV spot mag WD det 20 µm
UakW/rei 10.00 kV 3.5 5 000 x 11.7 mm BSED 238

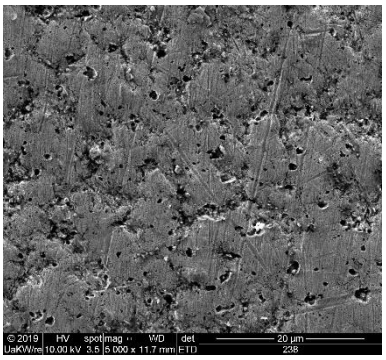

© 2019 HV spot mag WD det 20 µm
UakW/rei 10.00 kV 3.5 5 000 x 11.7 mm ETD 238

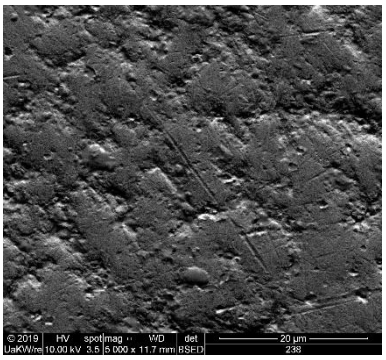

© 2019 HV spot mag WD det 20 µm
UakW/rei 10.00 kV 3.5 5 000 x 11.7 mm BSED 238

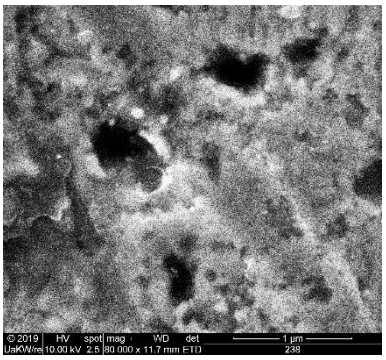

© 2019 HV spot mag WD det 5 µm
UakW/rei 10.00 kV 3.5 20 000 x 11.7 mm ETD 238

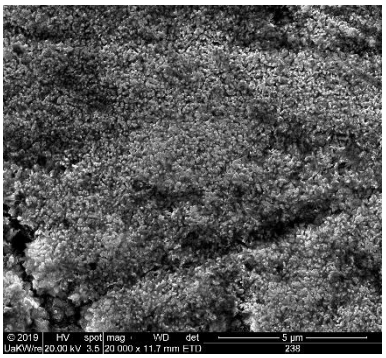

© 2019 HV spot mag WD det 1 µm
UakW/rei 10.00 kV 3.5 80 000 x 11.7 mm ETD 238

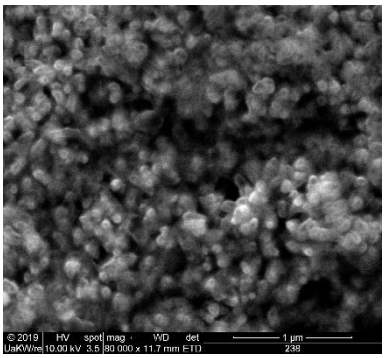

© 2019 HV spot mag WD det 5 µm
UakW/rei 10.00 kV 2.5 20 000 x 11.7 mm ETD 238


© 2019 HV spot mag WD det 20 µm
UakW/rei 10.00 kV 3.5 5 000 x 11.7 mm ETD 238


© 2019 HV spot mag WD det 20 µm
UakW/rei 10.00 kV 3.5 5 000 x 11.7 mm BSED 238

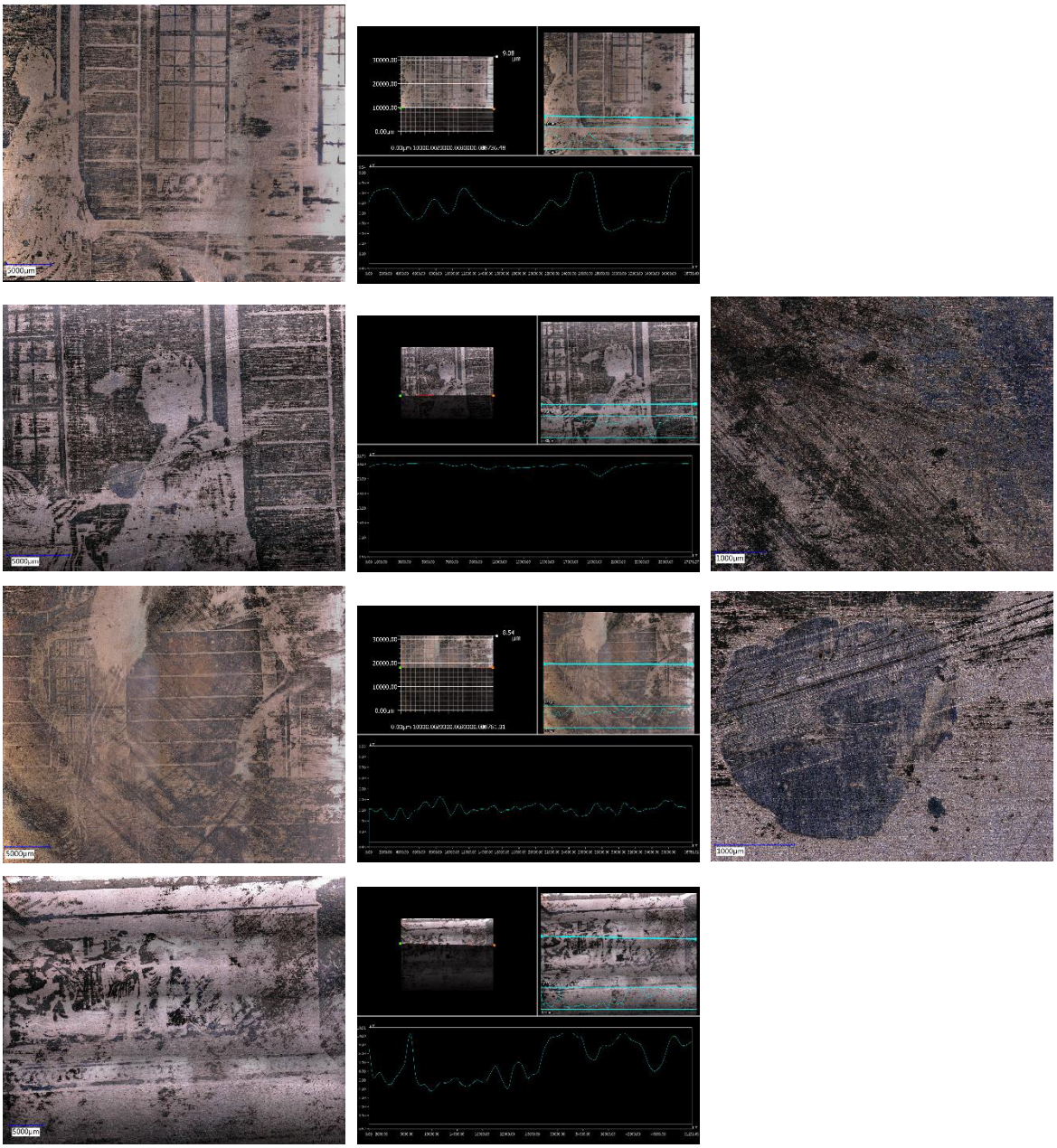

© 2019 HV spot mag WD det 1 µm
UakW/rei 10.00 kV 2.5 80 000 x 11.7 mm ETD 238


© 2019 HV spot mag WD det 5 µm
UakW/rei 20.00 kV 3.5 20 000 x 11.7 mm ETD 238

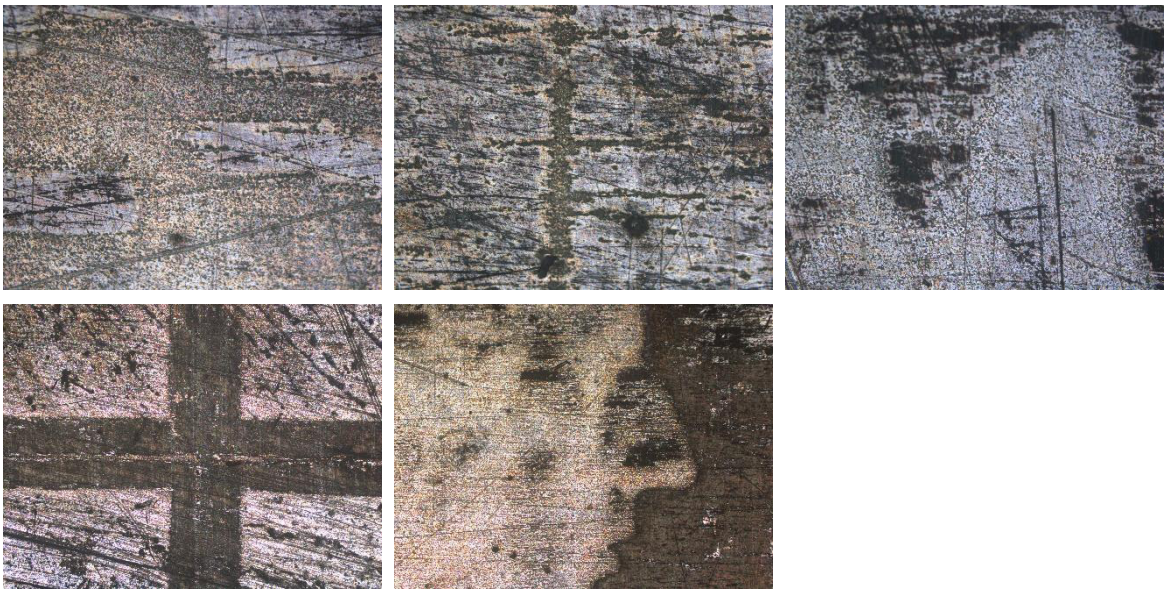

© 2019 HV spot mag WD det 1 µm
UakW/rei 10.00 kV 3.5 80 000 x 11.7 mm ETD 238

Element	Atomic%	Element	Atomic%	Element	Atomic%
C	38,97	C	37,26	C	37,37
O	4,37	O	8,05	O	20,86
Si	0,57	Si	0,68	Si	0,57
P	0,53	Ag	52,74	Ag	37,56
S	14,39	Cu	1,27	Cu	3,63
Cl	1,10				
Ag	38,72				
Cu	1,35				

Lichtmikroskopaufnahmen (z-Scans; Keyence, VHX-5000), Universität für Bodenkultur Wien



Lichtmikroskopaufnahmen (Olympus GX51, Happy Platting GmbH, Wiener Neustadt)



Inventarnr.: 83939/19 **Alte Inventarnr.:** MdA4, 238

Sammlungsgr.: 530 Metallbearbeitung

akt. Standort: Standorte-TMW/TMW-Museum/E5/3-102

Titel: Kupferdruckplatte

Hersteller_in: Theyer, Franz; Waidele, Erwin

Ort: Wien

Datierung: 1840 **bis** 1845

Maße:

Breite 30.6 cm

Tiefe 27 cm

Höhe 0.1 cm

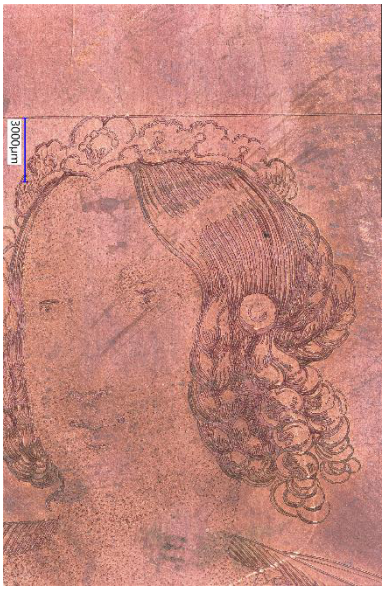
Beschreibung:

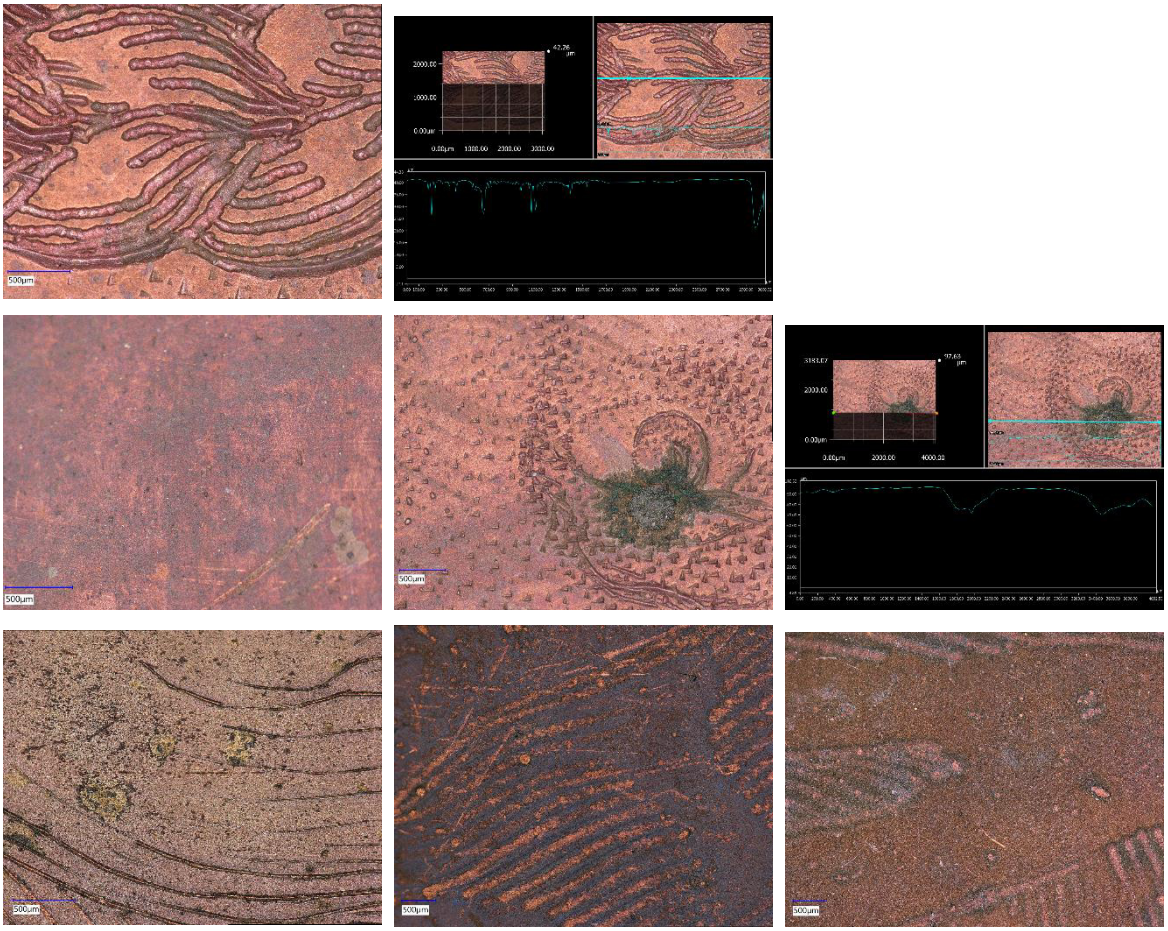
Befindet sich in Lade 3 (von oben gezählt) auf der mit schwarzem Stoff bespannten Tafel (dort befinden sich die Nummern 236-253).

Schlagworte: Kupfer, versilbert

Digitalverweise:

Lichtmikroskopaufnahmen (z-Scans; Keyence, VHX-5000), Universität für Bodenkultur Wien





Lichtmikroskopaufnahmen (Olympus GX51, Happy Platting GmbH, Wiener Neustadt)

Inventarnr.: 83939/20 **Alte Inventarnr.:** MdA4, 239

Sammlungsgr.: 530 Metallbearbeitung

akt. Standort: Standorte-TMW/TMW-Museum/E5/3-102

Titel: Kupferdruckplatte

Hersteller_in: Theyer, Franz; Waidele, Erwin

Ort: Wien

Datierung: 1840 **bis** 1845

Maße:

Breite 18 cm

Tiefe 13.3 cm

Höhe 0.2 cm

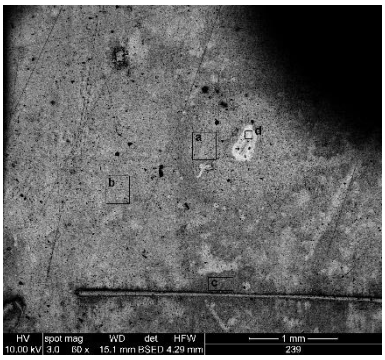
Beschreibung:

Befindet sich in Lade 3 (von oben gezählt) auf der mit schwarzem Stoff bespannten Tafel (dort befinden sich die Nummern 236-253).

Schlagworte: Kupfer, versilbert

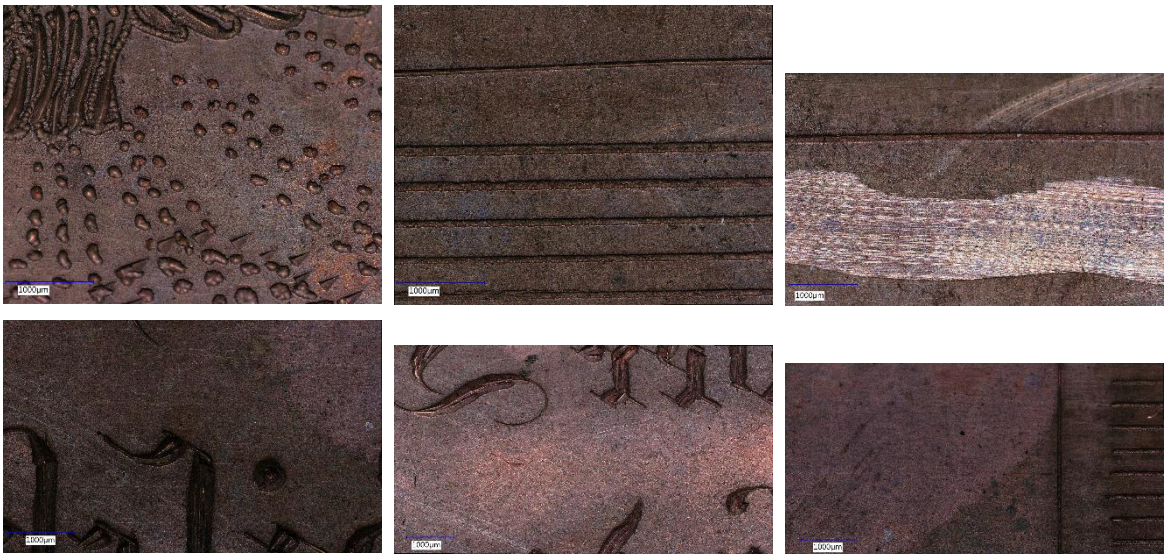
Digitalverweise:

REM, EDX (Zeiss, Universität für angewandte Kunst Wien)

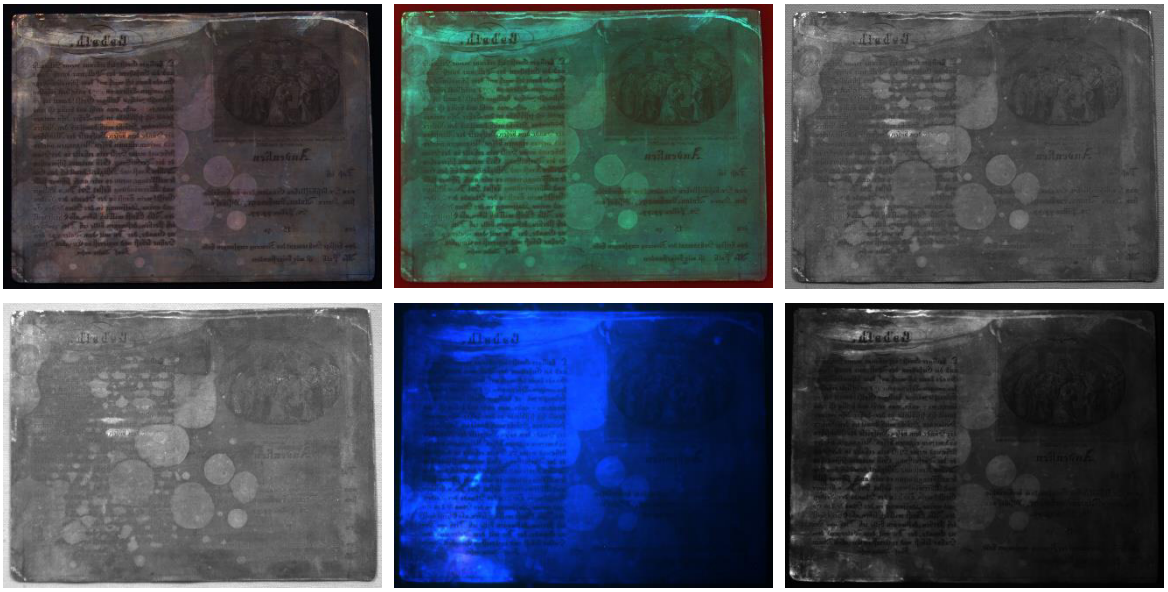


Element	Atomic%	Element	Atomic%
C	9,69	C	12,09
O	4,36	O	4,07
Cu	4,94	Cu	5,37
Ag	81,00	Ag	78,46

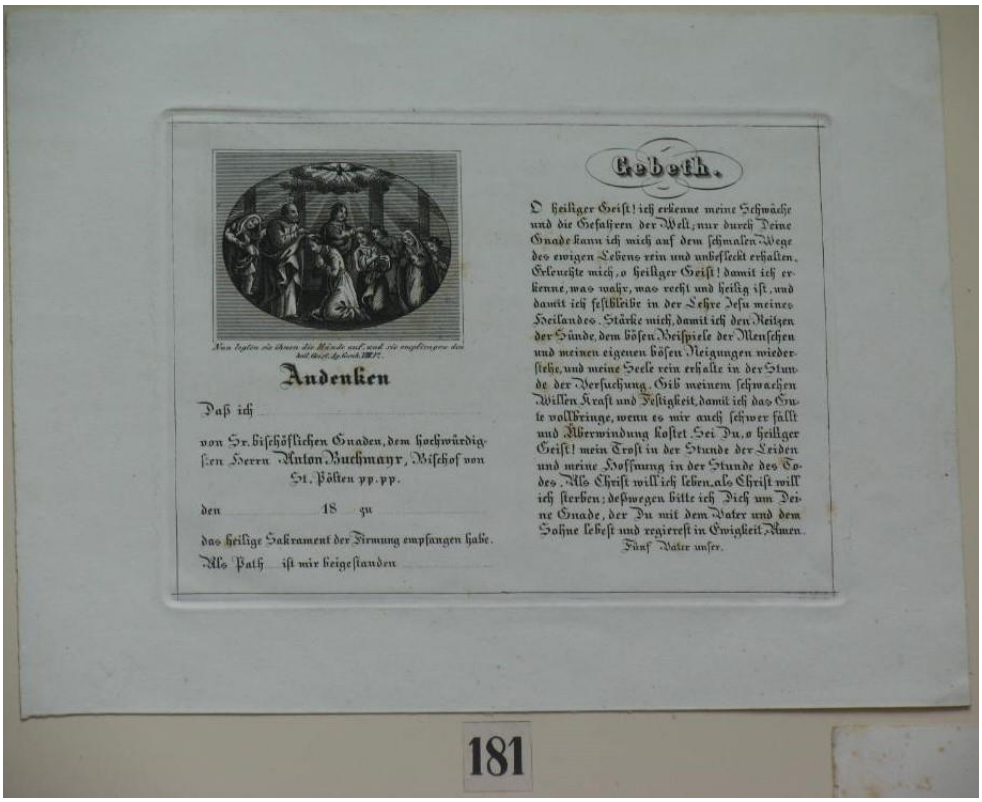
Lichtmikroskopaufnahmen (z-Scans; Keyence, VHX-5000), Universität für Bodenkultur Wien



Multispektralkamera, Rumänien



Druck auf Papier (TMW Archiv)



Nun legten sie ihnen die Hände auf, und sie empfingen den heil. Geist. Apgesch. VIII 17.

Andenken

Daß ich .....

von Sr. bischöflichen Gnaden, dem hochwürdigsten Herrn Anton Buchmayr, Bischof von St. Pölten pp. pp.

den ..... 18 .. zu .....

das heilige Sakrament der Firmung empfangen habe.

Als Path ..... ist mir beigestanden .....

Gebeth.

O heiliger Geist! ich erkenne meine Schwäche und die Gefahren der Welt; nur durch Deine Gnade kann ich mich auf dem schmalen Wege des ewigen Lebens rein und unbefleckt erhalten. Erleuchte mich, o heiliger Geist! damit ich erkenne, was wahr, was recht und heilig ist, und damit ich festbleibe in der Lehre Jesu meines Heilandes. Stärke mich, damit ich den Reizen der Sünde, dem bösen Beispiele der Menschen und meinen eigenen bösen Neigungen widerstehe, und meine Seele rein erhalte in der Stunde der Versuchung. Gib meinem schwachen Willen Kraft und Festigkeit, damit ich das Gute vollbringe, wenn es mir auch schwer fällt und Überwindung kostet. Sei Du, o heiliger Geist! mein Trost in der Stunde der Leiden und meine Hoffnung in der Stunde des Todes. Als Christ will ich leben, als Christ will ich sterben; deßwegen bitte ich Dich um Deine Gnade, der Du mit dem Vater und dem Sohne lebest und regierest in Ewigkeit. Amen.

Fünf Vater unser.

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Inventarnr.: 83939/21 **Alte Inventarnr.:** MdA4, 240

Sammlungsgr.: 530 Metallbearbeitung

akt. Standort: Standorte-TMW/TMW-Museum/E5/3-102

Titel: Kupferdruckplatte

Hersteller_in: Theyer, Franz; Waidele, Erwin

Ort: Wien

Datierung: 1840 **bis** 1845

Maße:

Breite 7.9 cm

Tiefe 11.2 cm

Höhe 0.1 cm

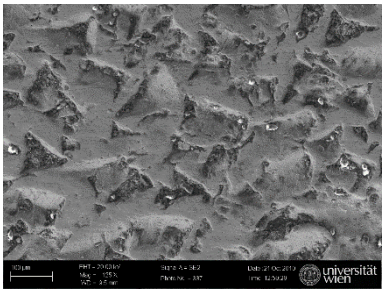
Beschreibung:

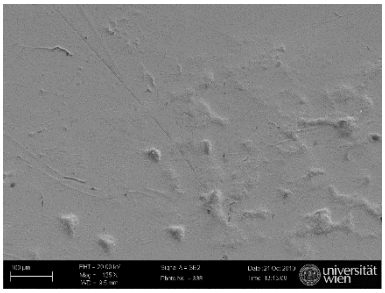
Befindet sich in Lade 3 (von oben gezählt) auf der mit schwarzem Stoff bespannten Tafel (dort befinden sich die Nummern 236-253).

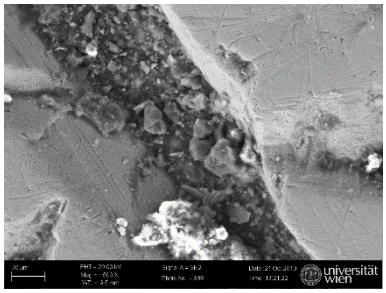
Schlagworte: Kupfer

Digitalverweise:

REM, EDX (Zeiss Supra 55 VP, Universität Wien)

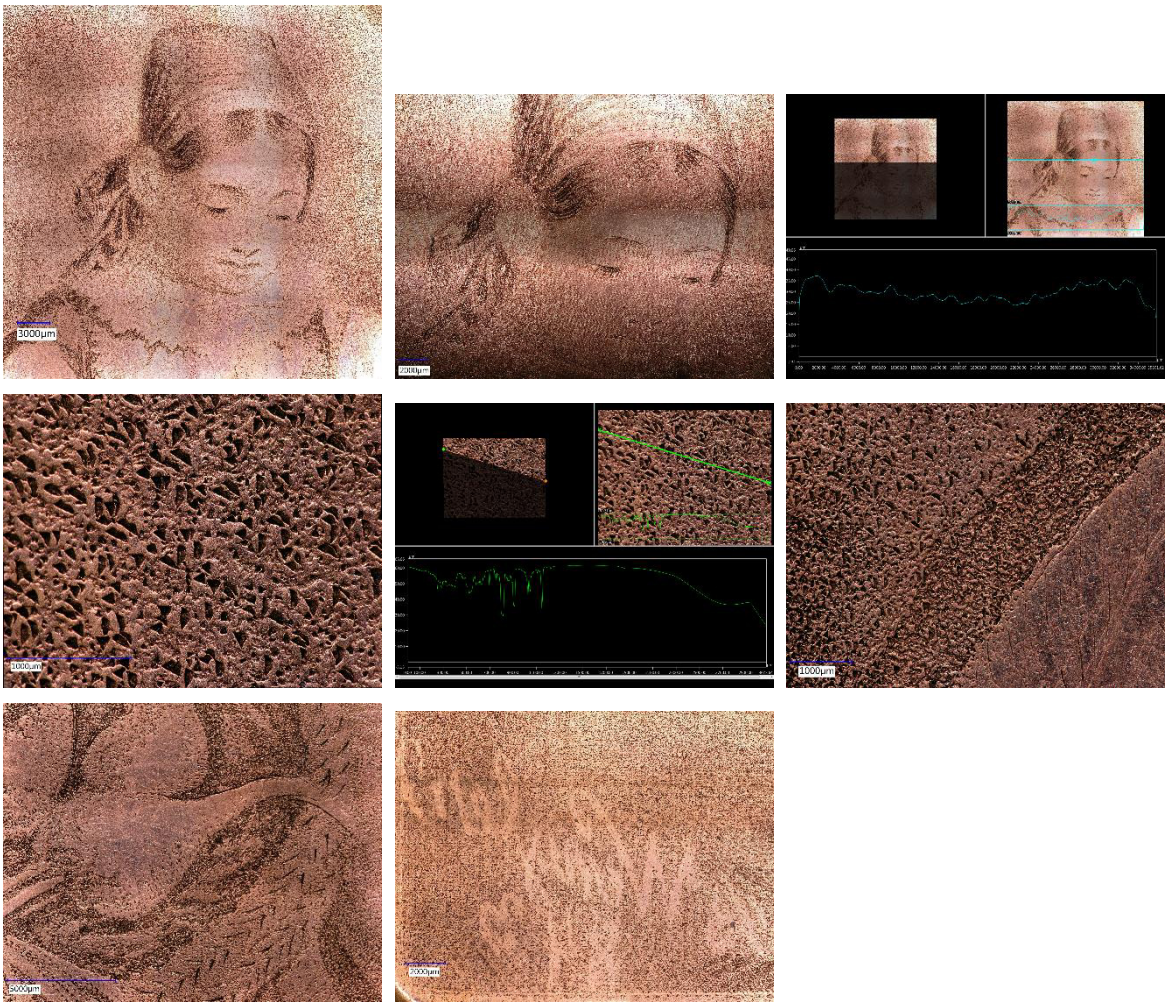






Element	Atomic%	Element	Atomic%	Element	Atomic%
C	64,19	C	47,61	C	66,17
O	18,73	O	14,59	O	27,98
Si	0,39	Cu	37,8	Si	1,31
S	0,13			Ag	0,43
K	0,15			P	0,42
Ca	0,44			S	0,12
Cu	15,97			K	0,71
				Ca	1,77
				Fe	0,33
				Cu	0,62

Lichtmikroskopaufnahmen (z-Scans; Keyence, VHX-5000), Universität für Bodenkultur Wien



Druck auf Papier (TMW Archiv)

Inventarnr.: 83939/22 **Alte Inventarnr.:** MdA4, 241

Sammlungsgr.: 530 Metallbearbeitung

akt. Standort: Standorte-TMW/TMW-Museum/E5/3-102

Titel: Kupferdruckplatte

Hersteller_in: Theyer, Franz; Waidele, Erwin

Ort: Wien

Datierung: 1840 **bis** 1845

Maße:

Breite 7.7 cm

Tiefe 11 cm

Höhe 0.1 cm

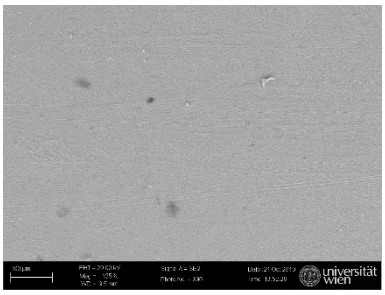
Beschreibung:

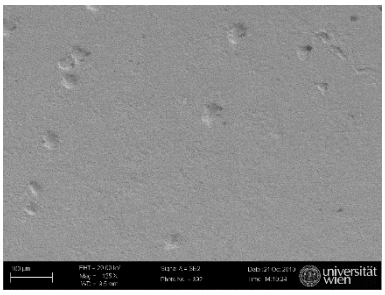
Befindet sich in Lade 3 (von oben gezählt) auf der mit schwarzem Stoff bespannten Tafel (dort befinden sich die Nummern 236-253).

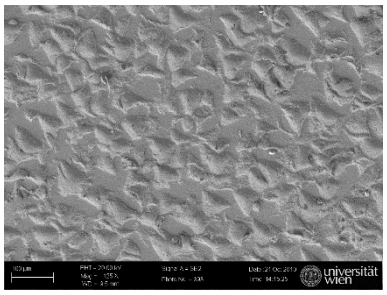
Schlagworte: Kupfer, versilbert

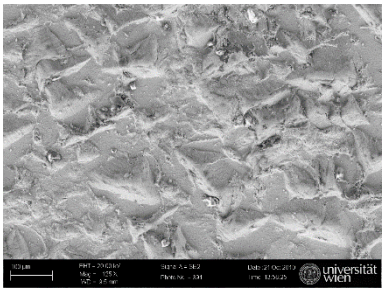
Digitalverweise:

REM, EDX (Zeiss Supra 55 VP, Universität Wien)



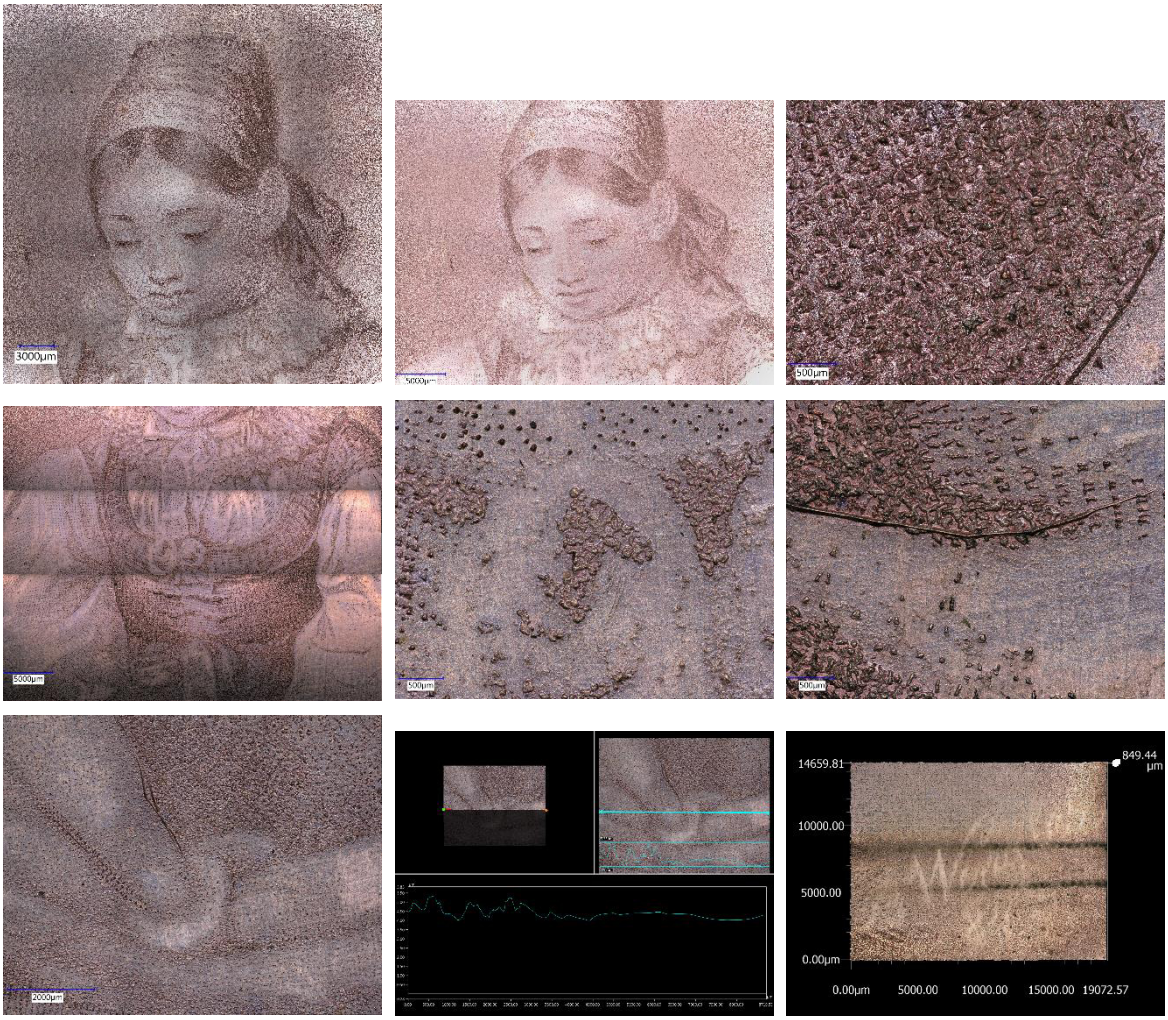


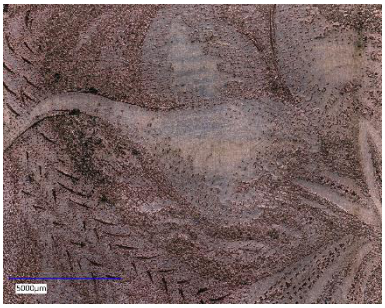


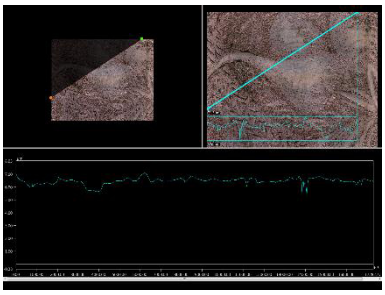
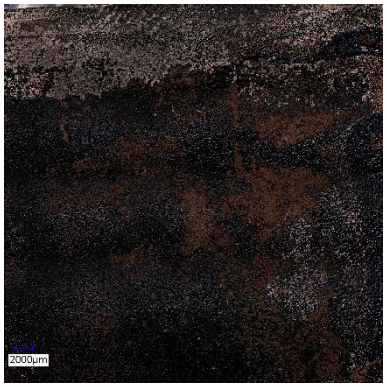


Element	Atomic %	Element	Atomic %	Element	Atomic %	Element	Atomic %	Element	Atomic %
C	39,64	C	58,64	C	42,98	C	50,38	C	49,71
O	18,59	O	20,2	O	18,61	O	16,38	O	20,06
Cu	36,01	Si	0,41	Cu	33	Cu	30,32	Si	0,17
Ag	5,75	S	0,44	Ag	5,41	Ag	2,92	Cl	0,18
		Cu	19					Cu	25,91
		Ag	1,31					Ag	3,97

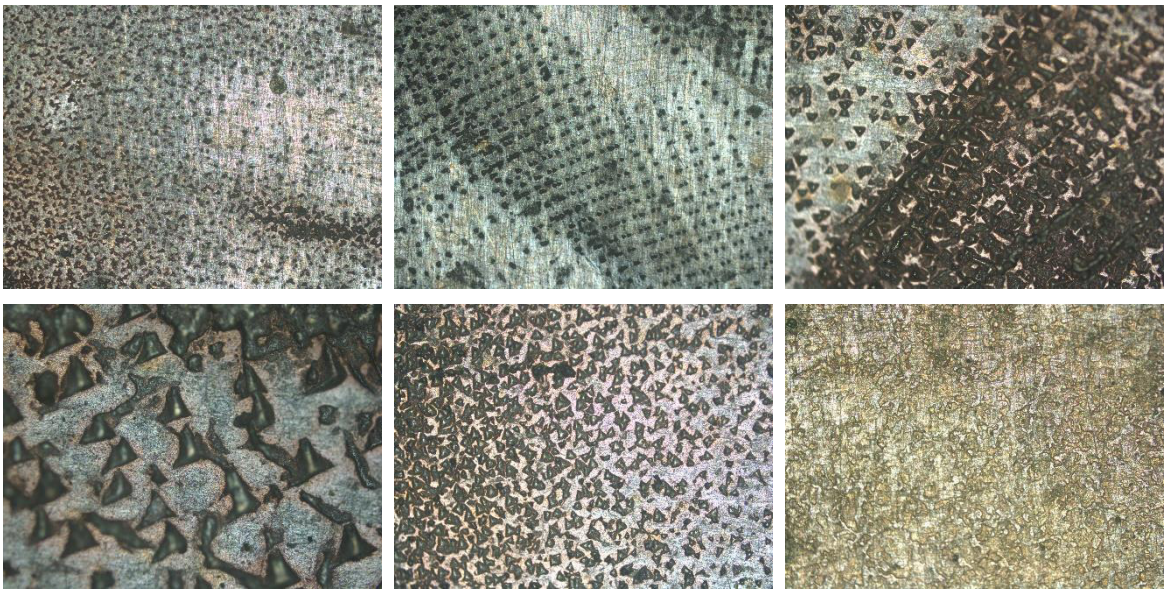
Lichtmikroskopaufnahmen (z-Scans; Keyence, VHX-5000), Universität für Bodenkultur Wien





Lichtmikroskopaufnahmen (Olympus GX51, Happy Platting GmbH, Wiener Neustadt)



Druck auf Papier (TMW Archiv)

Inventarnr.: 83939/23 **Alte Inventarnr.:** MdA4, 242

Sammlungsgr.: 530 Metallbearbeitung

akt. Standort: Standorte-TMW/TMW-Museum/E5/3-102

Titel: Kupferdruckplatte

Hersteller_in: Theyer, Franz; Waidele, Erwin

Ort: Wien

Datierung: 1840 **bis** 1845

Maße:

Breite 10.5 cm

Tiefe 6 cm

Höhe 0.1 cm

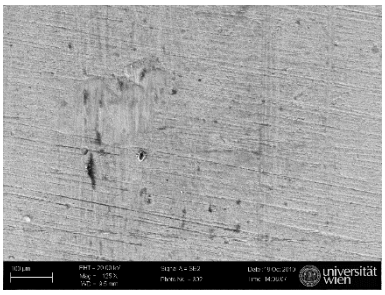
Beschreibung:

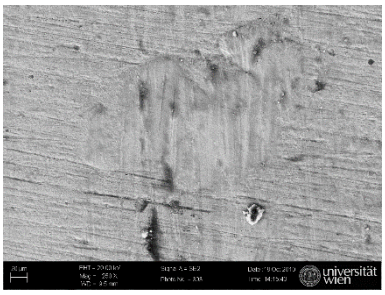
Befindet sich in Lade 3 (von oben gezählt) auf der mit schwarzem Stoff bespannten Tafel (dort befinden sich die Nummern 236-253).

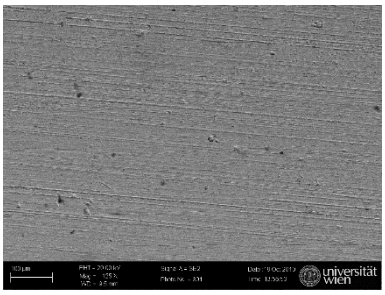
Schlagworte: Kupfer

Digitalverweise:

REM, EDX (Zeiss Supra 55 VP, Universität Wien)

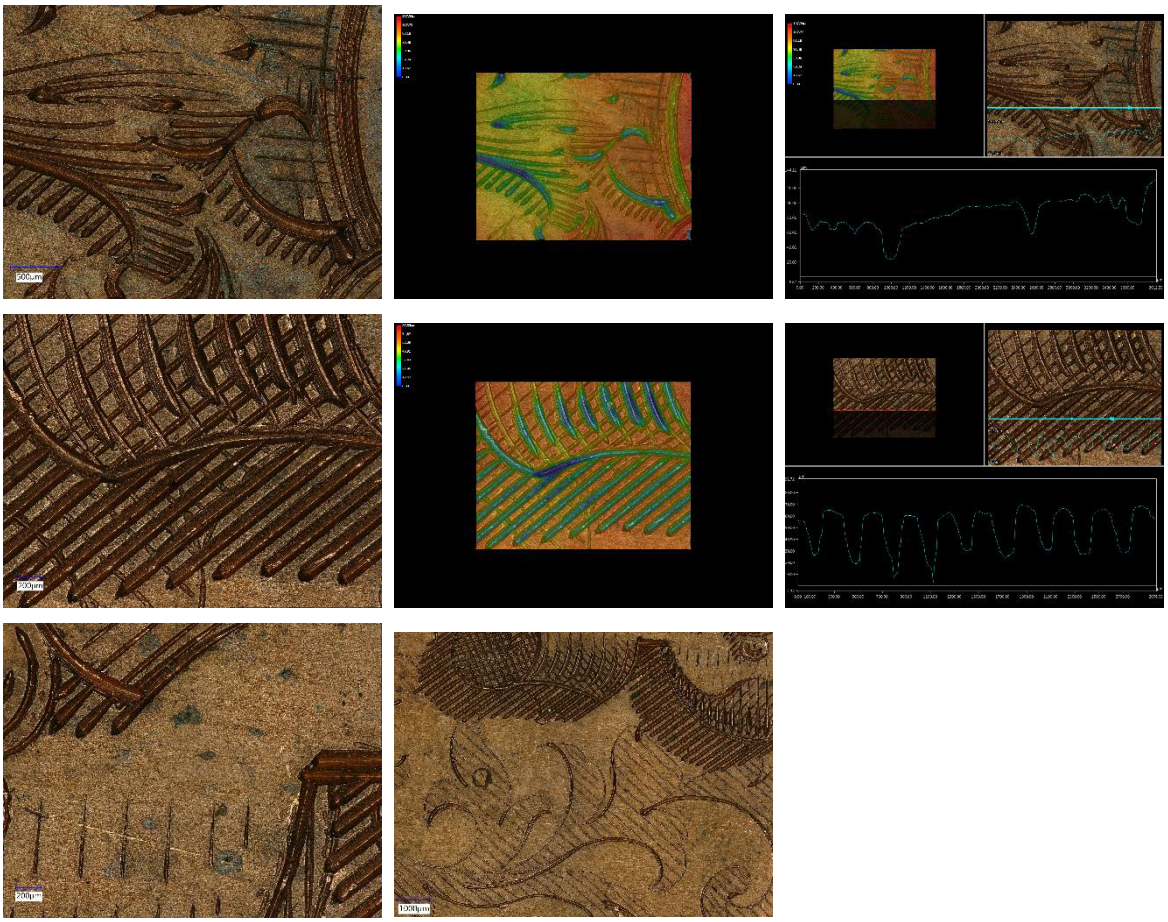






Element	Atomic%	Element	Atomic%
C	43,99	C	72,19
O	10,68	O	11,66
Cu	45,33	S	0,15
		Cu	16

Lichtmikroskopaufnahmen (z-Scans; Keyence, VHX-5000), Universität für Bodenkultur Wien



Inventarnr.: 83939/24 **Alte Inventarnr.:** MdA4, 243

Sammlungsgr.: 530 Metallbearbeitung

akt. Standort: Standorte-TMW/TMW-Museum/E5/3-102

Titel: Kupferdruckplatte

Hersteller_in: Theyer, Franz; Waidele, Erwin

Ort: Wien

Datierung: 1840 **bis** 1845

Maße:

Breite 6 cm

Tiefe 8.1 cm

Höhe 1 cm

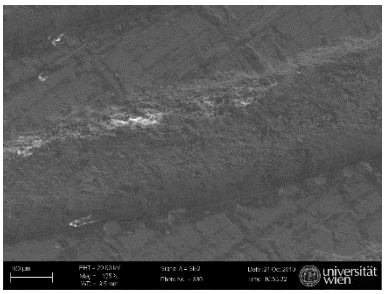
Beschreibung:

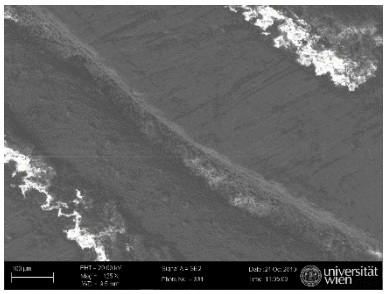
Befindet sich in Lade 3 (von oben gezählt) auf der mit schwarzem Stoff bespannten Tafel (dort befinden sich die Nummern 236-253).

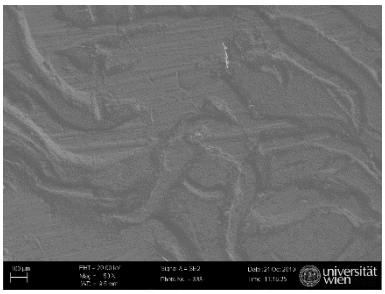
Schlagworte: Kupfer

Digitalverweise:

REM, EDX (Zeiss Supra 55 VP, Universität Wien)

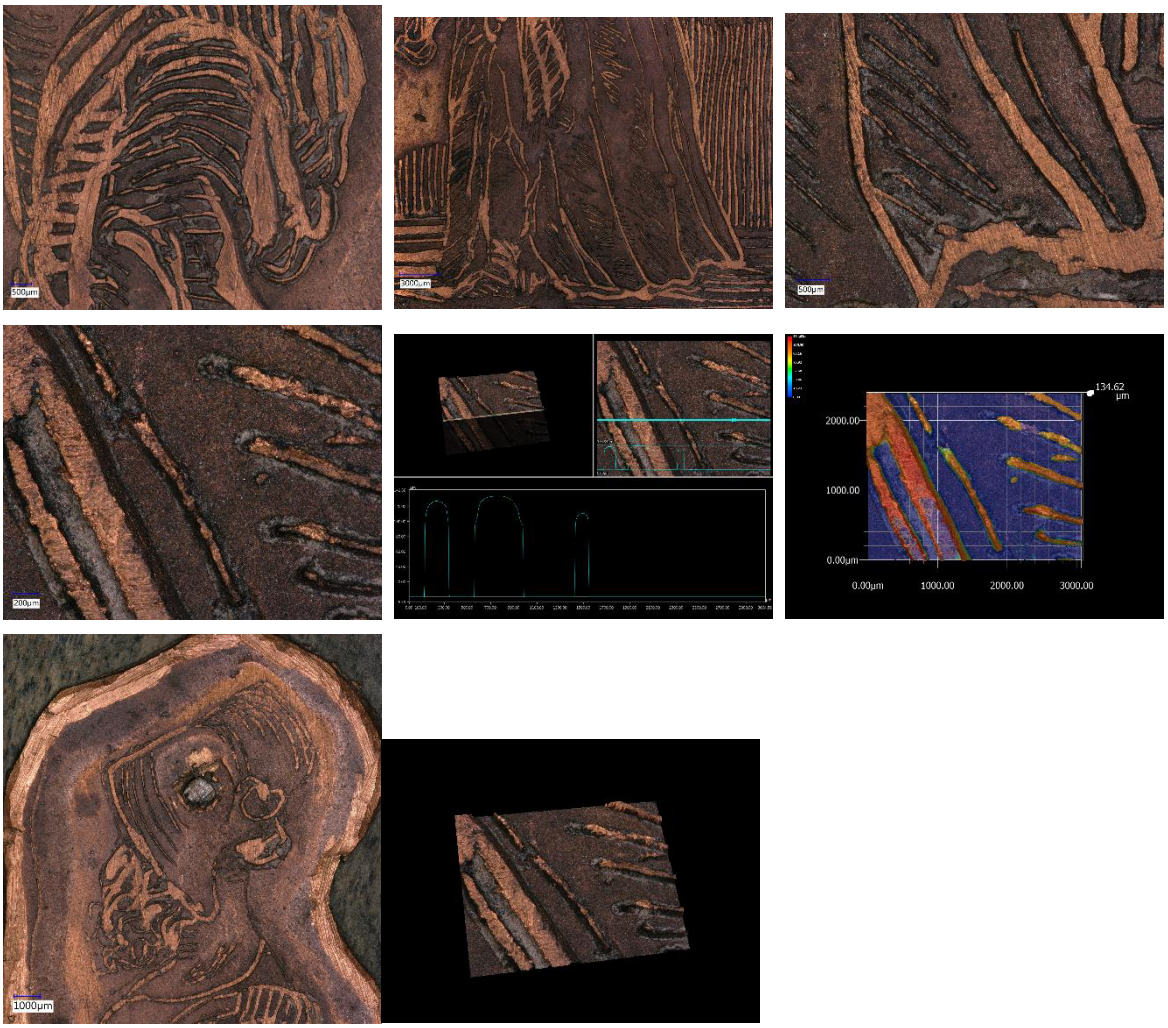






Element	Atomic%	Element	Atomic%	Element	Atomic%
C	55,87	C	55,59	C	41,73
O	25,75	O	28,11	O	40,93
Al	1,56	Al	1,13	Al	3,56
Si	2,27	Si	1,77	Si	6,09
S	0,19	S	0,54	S	0,55
K	0,38	K	0,35	Cl	0,13
Cu	13,97	Fe	0,14	K	1,26
		Cu	12,37	Ca	0,24
				Fe	0,44
				Cu	5,07
				C	41,73

Lichtmikroskopaufnahmen (z-Scans; Keyence, VHX-5000), Universität für Bodenkultur Wien



Inventarnr.: 83939/25 **Alte Inventarnr.:** MdA4, 244

Sammlungsgr.: 530 Metallbearbeitung

akt. Standort: Standorte-TMW/TMW-Museum/E5/3-102

Titel: Kupferdruckplatte

Hersteller_in: Theyer, Franz; Waidele, Erwin

Ort: Wien

Datierung: 1840 **bis** 1845

Maße:

Breite 5.8 cm

Tiefe 8.8 cm

Höhe 1 cm

Beschreibung:

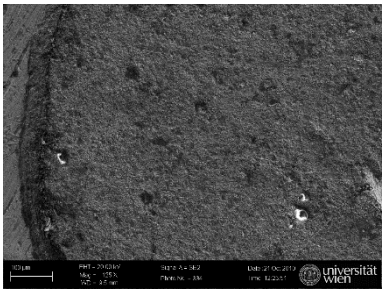
Befindet sich in Lade 3 (von oben gezählt) auf der mit schwarzem Stoff bespannten Tafel (dort befinden sich die Nummern 236-253).

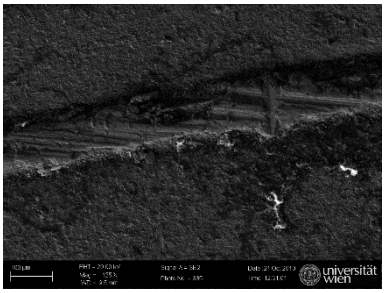
Schlagworte: Kupfer

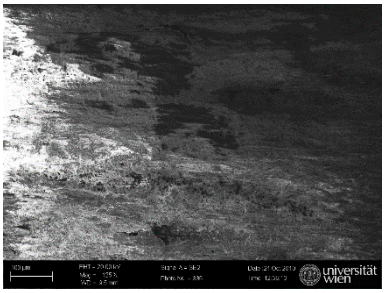
Digitalverweise:

REM, EDX (Zeiss Supra 55 VP, Universität Wien)

Holz

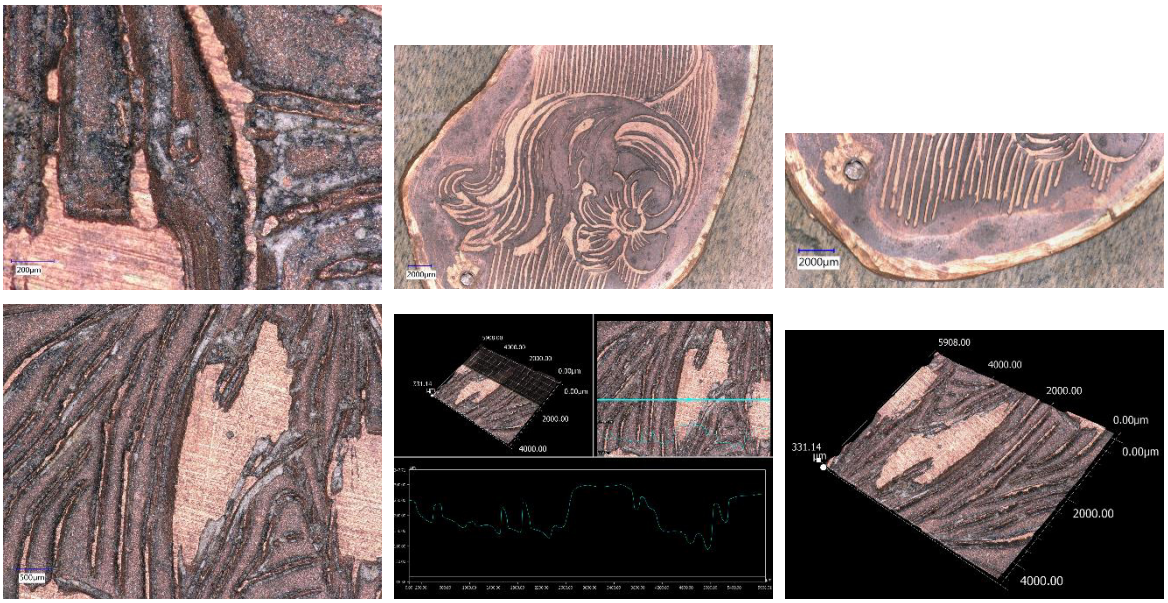






Element	Atomic%	Element	Atomic%	Element	Atomic%
C	58,17	C	58,62	C	49,53
O	23,91	O	26,08	O	48,52
Al	0,79	Al	1,01	Mg	0,19
Si	0,97	Si	1,35	Al	0,78
S	0,3	S	0,32	Si	0,89
K	0,21	K	0,27	K	0,06
Fe	0,11	Cu	12,36	Cu	0,03
Cu	15,53				

Lichtmikroskopaufnahmen (z-Scans; Keyence, VHX-5000), Universität für Bodenkultur Wien



Inventarnr.: 83939/26 **Alte Inventarnr.:** MdA4, 245

Sammlungsgr.: 530 Metallbearbeitung

akt. Standort: Standorte-TMW/TMW-Museum/E5/3-102

Titel: Kupferdruckplatte

Hersteller_in: Theyer, Franz; Waidele, Erwin

Ort: Wien

Datierung: 1840 **bis** 1845

Maße:

Breite 19.2 cm

Tiefe 6.8 cm

Höhe 0.1 cm

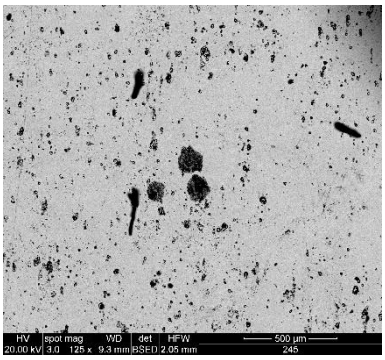
Beschreibung:

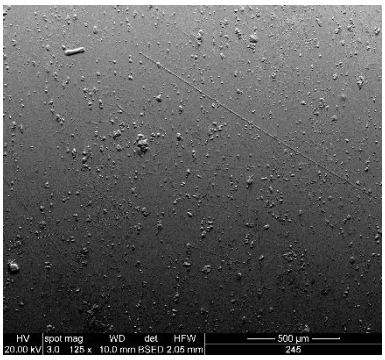
Befindet sich in Lade 3 (von oben gezählt) auf der mit schwarzem Stoff bespannten Tafel (dort befinden sich die Nummern 236-253).

Schlagworte: Kupfer, versilbert

Digitalverweise:

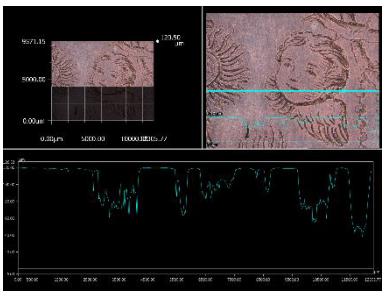
REM, EDX (Zeiss, Universität für angewandte Kunst Wien))

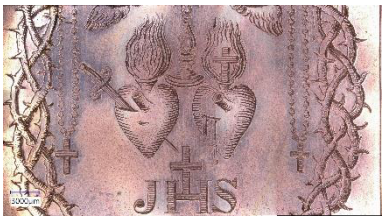


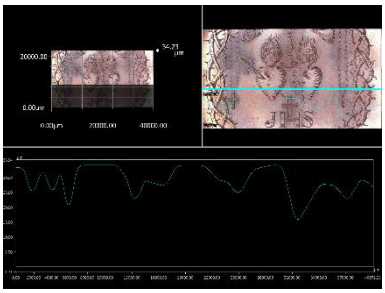


Element	Atomic%	Element	Atomic%
C	8,11	C	12,85
O	3,05	O	16,07
		Na	2,49
		Cl	0,67
		Ag	2,79
Ag	2,74	K	0,63
Cu	86,1	Cu	64,5

Lichtmikroskopaufnahmen (z-Scans; Keyence, VHX-5000), Universität für Bodenkultur Wien



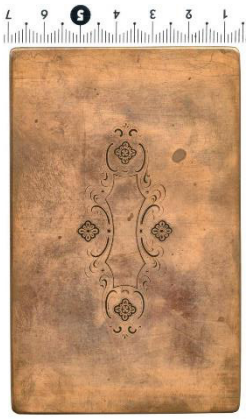




Inventarnr.: 83939/27 **Alte Inventarnr.:** MdA4, 246

Sammlungsgr.: 530 Metallbearbeitung

akt. Standort: Standorte-TMW/TMW-Museum/E5/3-102



Titel: Kupferdruckplatte

Hersteller_in: Theyer, Franz; Waidele, Erwin

Ort: Wien

Datierung: 1840 **bis** 1845

Maße:

Breite 10.2 cm

Tiefe 6.5 cm

Höhe 0.1 cm

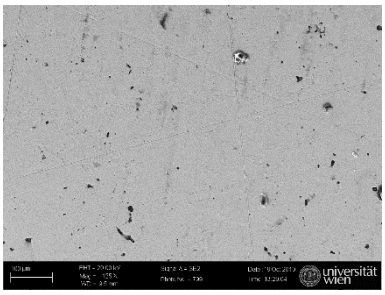
Beschreibung:

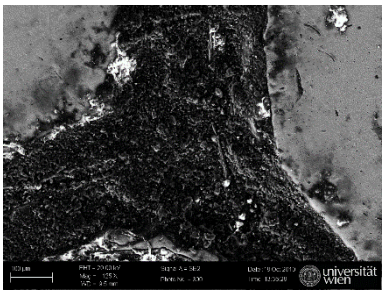
Befindet sich in Lade 3 (von oben gezählt) auf der mit schwarzem Stoff bespannten Tafel (dort befinden sich die Nummern 236-253).

Schlagworte: Kupfer

Digitalverweise:

REM, EDX (Zeiss Supra 55 VP, Universität Wien)





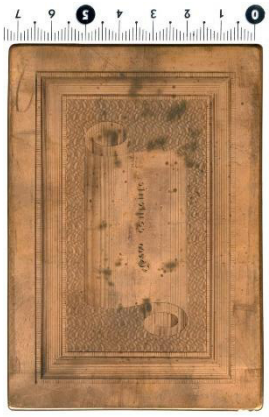
Element	Atomic%	Element	Atomic%
C	49,74	C	67,21
O	14,04	O	27,94
Cu	36,22	Al	0,37
		Si	1,31
		P	0,47
		K	0,73
		Ca	1,13
		Cu	0,84

Lichtmikroskopaufnahmen (z-Scans; Keyence, VHX-5000), Universität für Bodenkultur Wien

Inventarnr.: 83939/28 **Alte Inventarnr.:** MdA4, 247

Sammlungsgr.: 530 Metallbearbeitung

akt. Standort: Standorte-TMW/TMW-Museum/E5/3-102



Titel: Kupferdruckplatte

Hersteller_in: Theyer, Franz; Waidele, Erwin

Ort: Wien

Datierung: 1840 **bis** 1845

Maße:

Breite 10.8 cm

Tiefe 7.5 cm

Höhe 0.1 cm

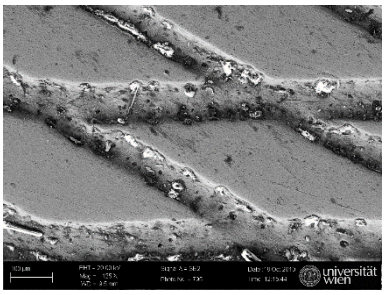
Beschreibung:

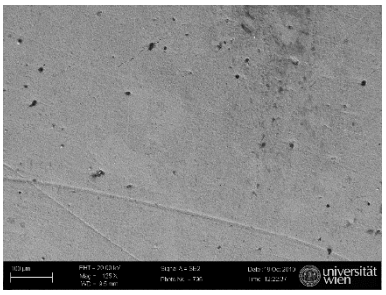
Befindet sich in Lade 3 (von oben gezählt) auf der mit schwarzem Stoff bespannten Tafel (dort befinden sich die Nummern 236-253).

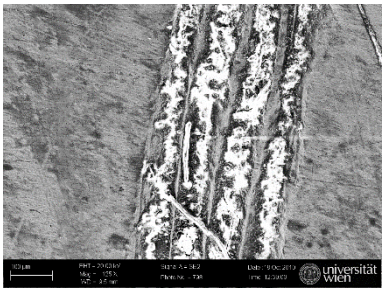
Schlagworte: Kupfer

Digitalverweise:

REM, EDX (Zeiss Supra 55 VP, Universität Wien)

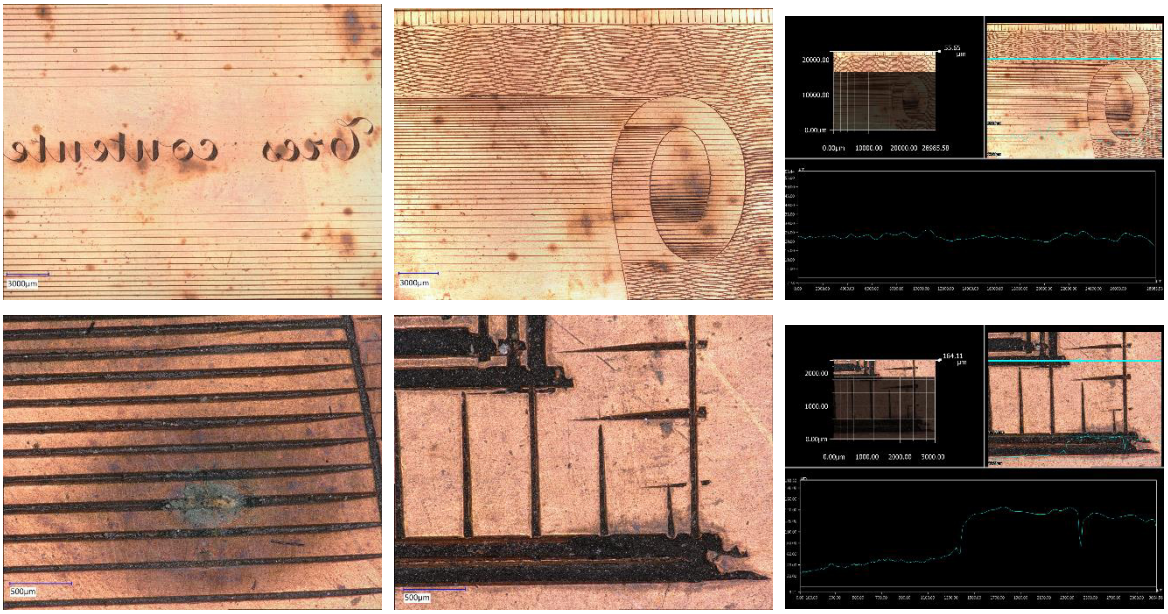






Element	Atomic%	Element	Atomic%	Element	Atomic%	Element	Atomic%
C	59,11	C	62,76	C	69,43	C	58,98
O	19,17	O	16,36	O	20,45	O	30,58
Si	0,42	S	0,19	Si	0,36	Al	0,48
S	0,39	Cu	20,69	S	0,47	Si	3,03
Ca	0,18			Cu	9,29	S	0,78
Cu	20,73					Ca	0,27
						Fe	0,62
						Cu	5,27

Lichtmikroskopaufnahmen (z-Scans; Keyence, VHX-5000), Universität für Bodenkultur Wien



Inventarnr.: 83939/29 **Alte Inventarnr.:** MdA4, 248

Sammlungsgr.: 530 Metallbearbeitung

akt. Standort: Standorte-TMW/TMW-Museum/E5/3-102

Titel: Druckplatte

Hersteller_in: Theyer, Franz; Waidele, Erwin

Ort: Wien

Datierung: 1840 **bis** 1845

Maße:

Breite 9 cm

Tiefe 5.5 cm

Höhe 0.1 cm

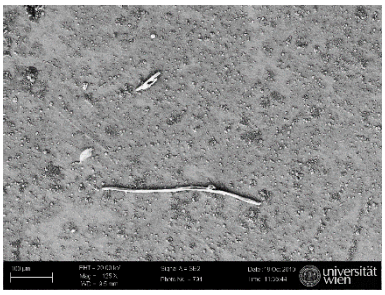
Beschreibung:

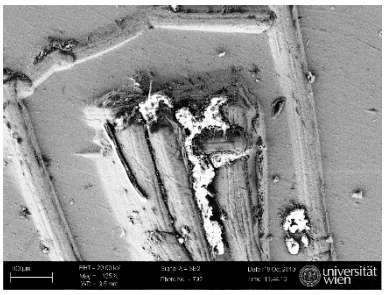
Befindet sich in Lade 3 (von oben gezählt) auf der mit schwarzem Stoff bespannten Tafel (dort befinden sich die Nummern 236-253).

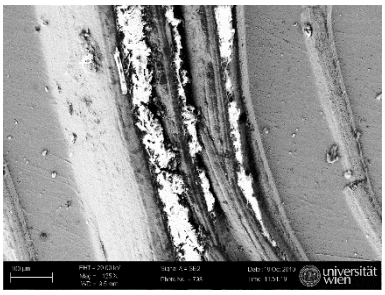
Schlagworte: Kupfer, versilbert

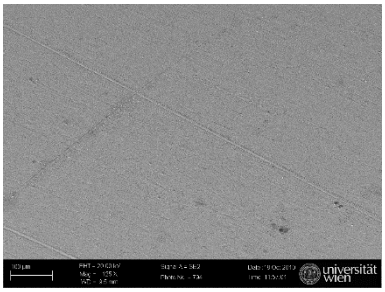
Digitalverweise:

REM, EDX (Zeiss Supra 55 VP, Universität Wien)



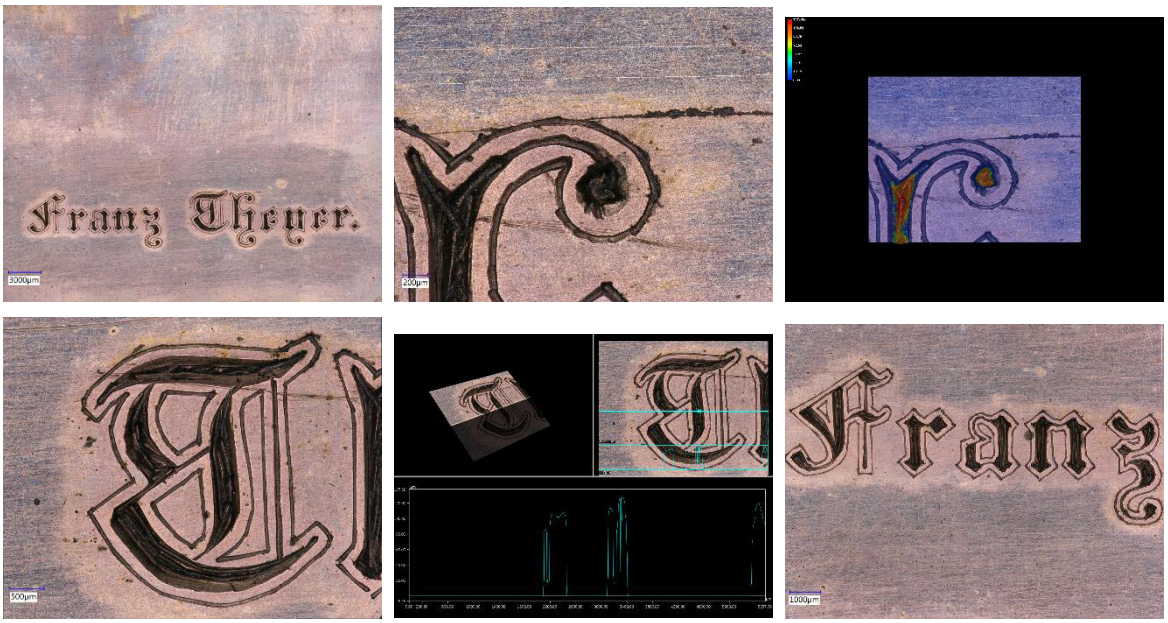






Element	Atomic%	Element	Atomic%	Element	Atomic%	Element	Atomic%
C	64,82	C	58,61	C	54,77	C	43,52
O	14,23	O	26,59	O	33,6	O	12,77
S	0,95	Si	0,42	Si	0,89	Cu	40,6
Cu	19,73	S	0,41	S	0,45	Ag	3,11
Ag	0,27	Cl	0,29	Cl	0,35		
		Ca	0,41	Ca	0,59		
		Cu	12,6	Cu	8,94		
		Ag	0,67	Ag	0,41		

Lichtmikroskopaufnahmen (z-Scans; Keyence, VHX-5000), Universität für Bodenkultur Wien



Inventarnr.: 83939/30 **Alte Inventarnr.:** MdA4, 249

Sammlungsgr.: 530 Metallbearbeitung

akt. Standort: Standorte-TMW/TMW-Museum/E5/3-102

Titel: Kupferdruckplatte

Hersteller_in: Theyer, Franz; Waidele, Erwin

Ort: Wien

Datierung: 1840 **bis** 1845

Maße:

Breite 9.1 cm

Tiefe 5.9 cm

Höhe 0.1 cm

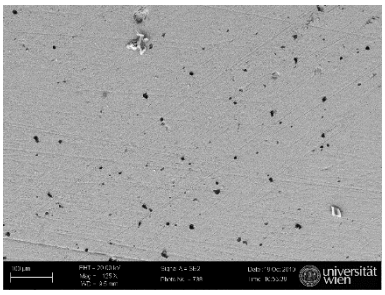
Beschreibung:

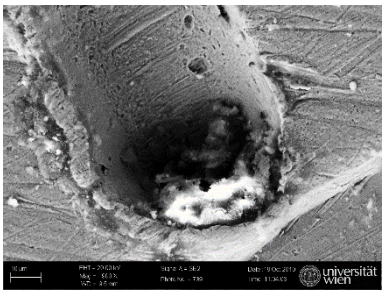
Befindet sich in Lade 3 (von oben gezählt) auf der mit schwarzem Stoff bespannten Tafel (dort befinden sich die Nummern 236-253).

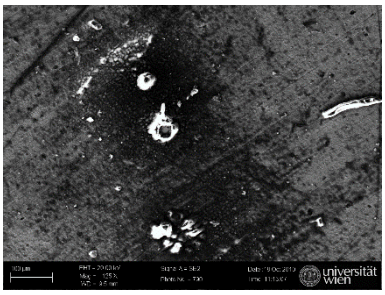
Schlagworte: Kupfer

Digitalverweise:

REM, EDX (Zeiss Supra 55 VP, Universität Wien)

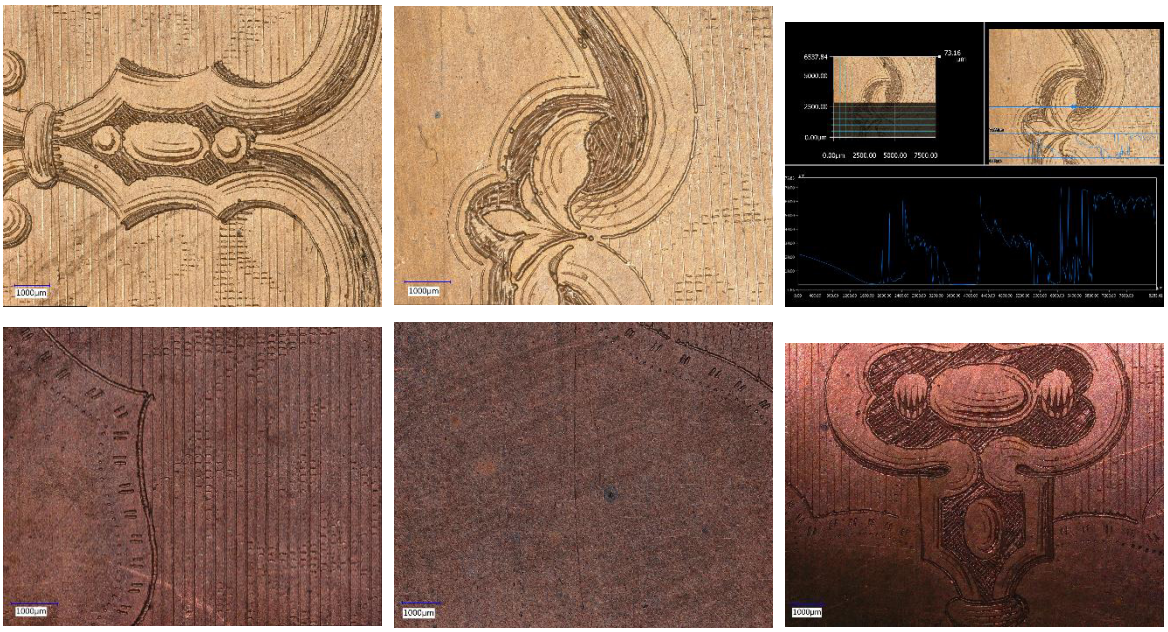






Element	Atomic%	Element	Atomic%	Element	Atomic%
C	47,92	C	64,22	C	76,78
O	11,48	O	11,71	O	15,39
Cu	40,6	S	0,24	S	0,22
		K	0,17	Cu	7,61
		Ca	0,22		
		Cu	23,44		

Lichtmikroskopaufnahmen (z-Scans; Keyence, VHX-5000), Universität für Bodenkultur Wien



Inventarnr.: 83939/31 **Alte Inventarnr.:** MdA4, 250

Sammlungsgr.: 530 Metallbearbeitung

akt. Standort: Standorte-TMW/TMW-Museum/E5/3-102

Titel: Kupferdruckplatte

Hersteller_in: Theyer, Franz; Waidele, Erwin

Ort: Wien

Datierung: 1840 **bis** 1845

Maße:

Breite 9.1 cm

Tiefe 5.9 cm

Höhe 0.1 cm

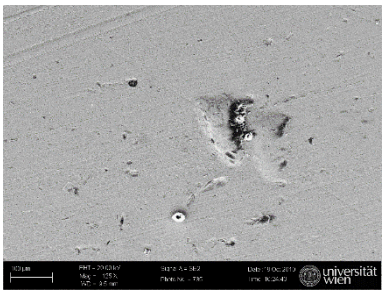
Beschreibung:

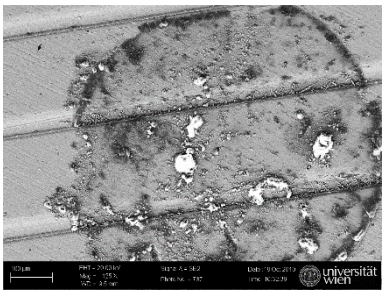
Befindet sich in Lade 3 (von oben gezählt) auf der mit schwarzem Stoff bespannten Tafel (dort befinden sich die Nummern 236-253).

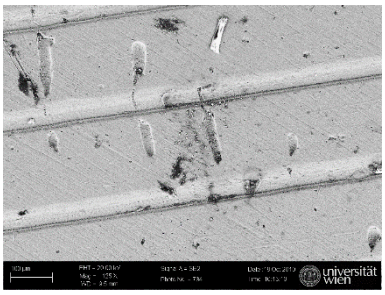
Schlagworte: Kupfer

Digitalverweise:

REM, EDX (Zeiss Supra 55 VP, Universität Wien)







Element	Atomic%	Element	Atomic%	Element	Atomic%
C	46,04	C	50,86	C	50,12
O	17,61	O	15,37	O	32,56
Cu	36,35	Cu	33,77	S	0,36
				Cl	0,48
				K	0,59
				Cu	15,88

Lichtmikroskopaufnahmen (z-Scans; Keyence, VHX-5000), Universität für Bodenkultur Wien

Inventarnr.: 83939/32 **Alte Inventarnr.:** MdA4, 251

Sammlungsgr.: 530 Metallbearbeitung

akt. Standort: Standorte-TMW/TMW-Museum/E5/3-102

Titel: Kupferdruckplatte

Hersteller_in: Theyer, Franz; Waidele, Erwin

Ort: Wien

Datierung: 1840 **bis** 1845

Maße:

Breite 9.8 cm

Tiefe 5.6 cm

Höhe 0.1 cm

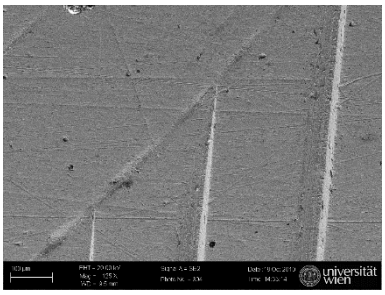
Beschreibung:

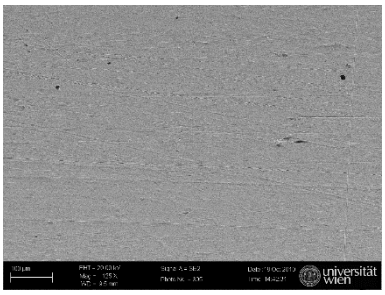
Befindet sich in Lade 3 (von oben gezählt) auf der mit schwarzem Stoff bespannten Tafel (dort befinden sich die Nummern 236-253).

Schlagworte: Kupfer

Digitalverweise:

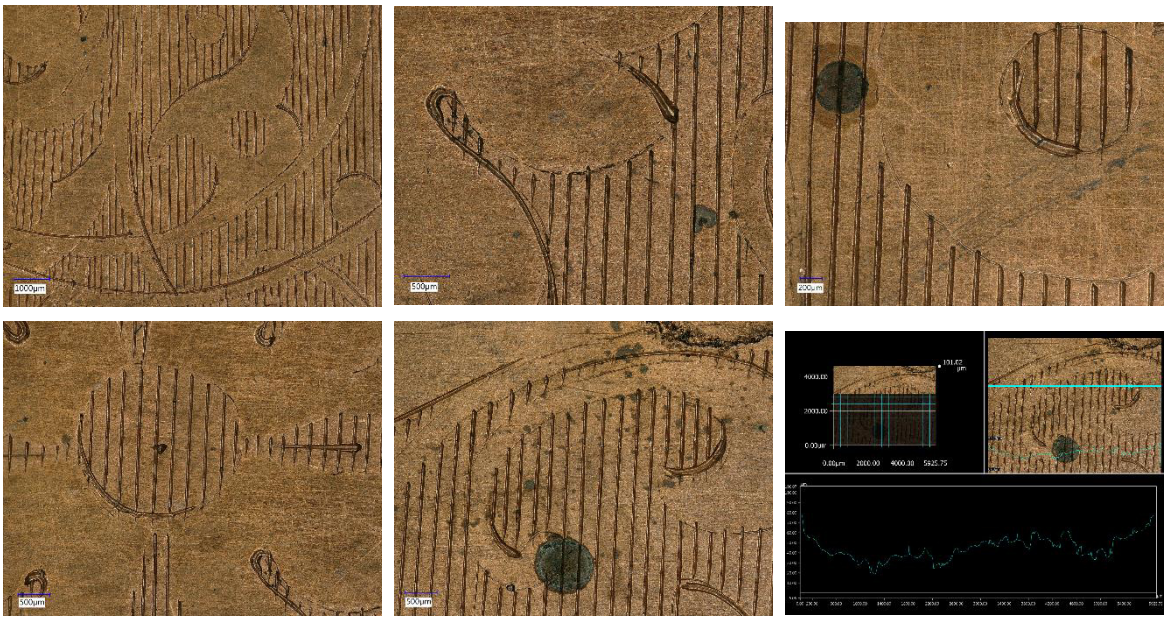
REM, EDX (Zeiss Supra 55 VP, Universität Wien)





Element	Atomic%
C	44,53
O	10,47
Cu	45

Lichtmikroskopaufnahmen (z-Scans; Keyence, VHX-5000), Universität für Bodenkultur Wien



Inventarnr.: 83939/33 **Alte Inventarnr.:** MdA4, 252

Sammlungsgr.: 530 Metallbearbeitung

akt. Standort: Standorte-TMW/TMW-Museum/E5/3-102

Titel: Druckplatte

Hersteller_in: Theyer, Franz; Waidele, Erwin

Ort: Wien

Datierung: 1840 **bis** 1845

Maße:

Breite 30.4 cm

Tiefe 16.8 cm

Höhe 0.1 cm

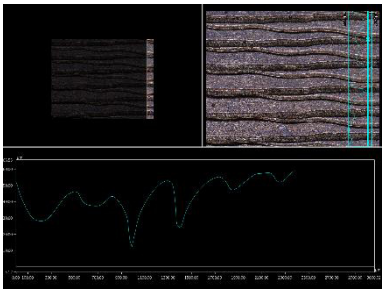
Beschreibung:

Befindet sich in Lade 3 (von oben gezählt) auf der mit schwarzem Stoff bespannten Tafel (dort befinden sich die Nummern 236-253).

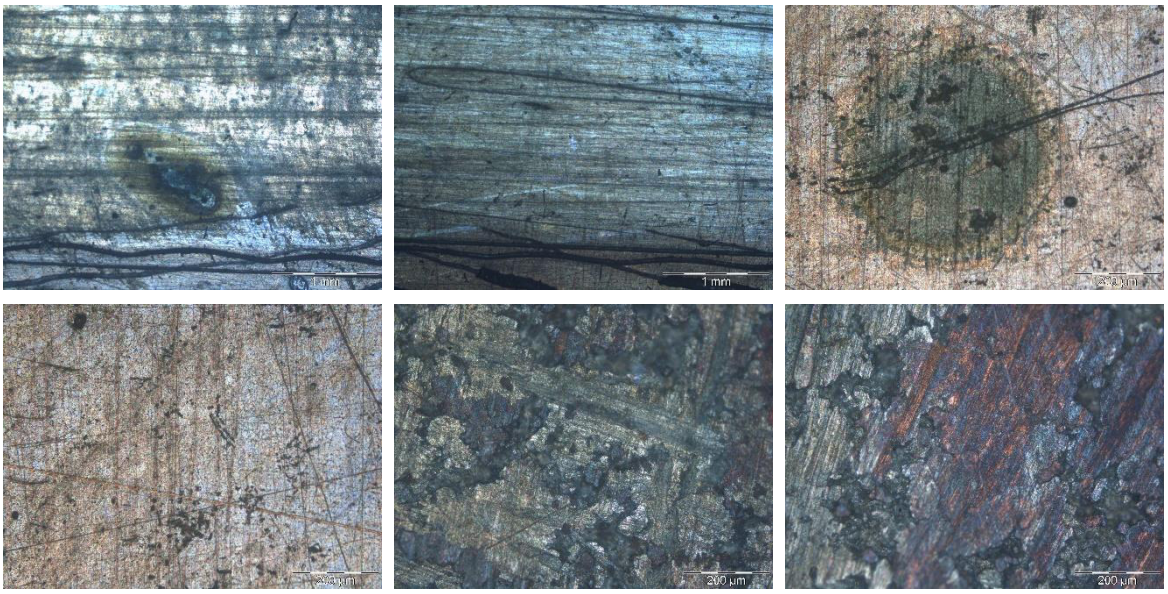
Schlagworte: Kupfer, versilbert

Digitalverweise:

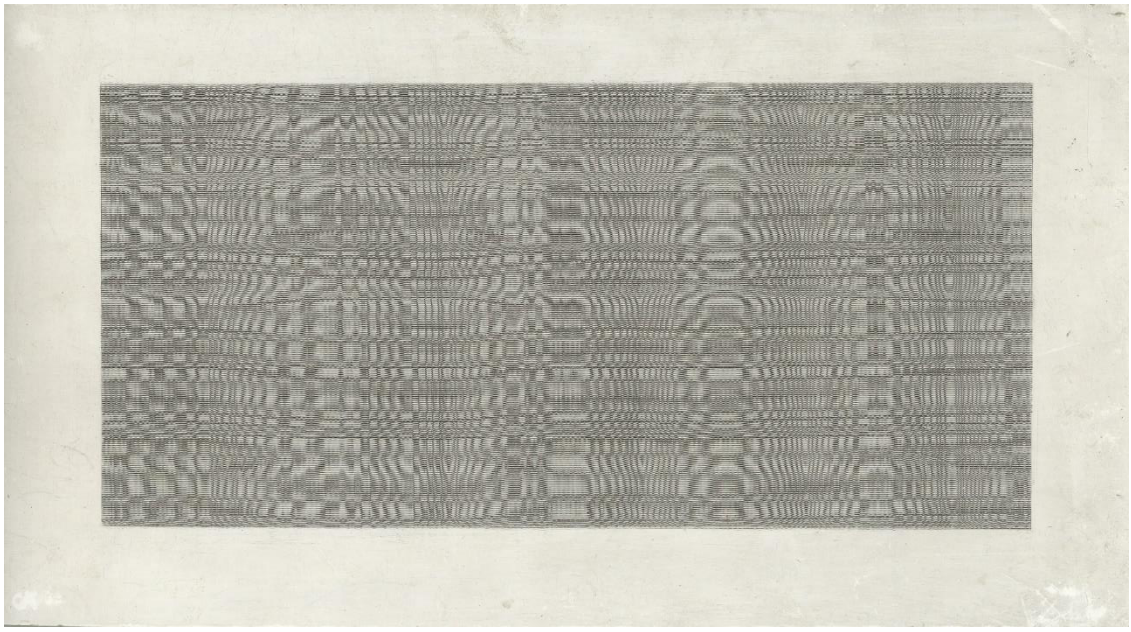
Lichtmikroskopaufnahmen (z-Scans; Keyence, VHX-5000), Universität für Bodenkultur Wien



Lichtmikroskopaufnahmen (Olympus GX51, Happy Platting GmbH, Wiener Neustadt)



Druck auf Papier (TMW Archiv)



Inventarnr.: 83939/34 **Alte Inventarnr.:** MdA4, 253

Sammlungsgr.: 530 Metallbearbeitung

akt. Standort: Standorte-TMW/TMW-Museum/E5/3-102

Titel: Kupferdruckplatte

Hersteller_in: Theyer, Franz; Waidele, Erwin

Ort: Wien

Datierung: 1840 **bis** 1845

Maße:

Breite 8.9 cm

Tiefe 5.6 cm

Höhe 0.1 cm

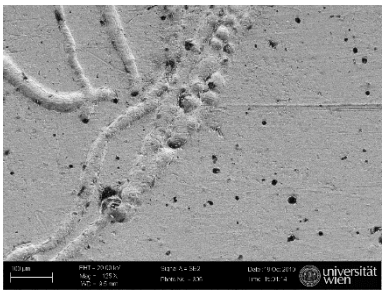
Beschreibung:

Befindet sich in Lade 3 (von oben gezählt) auf der mit schwarzem Stoff bespannten Tafel (dort befinden sich die Nummern 236-253).

Schlagworte: Kupfer

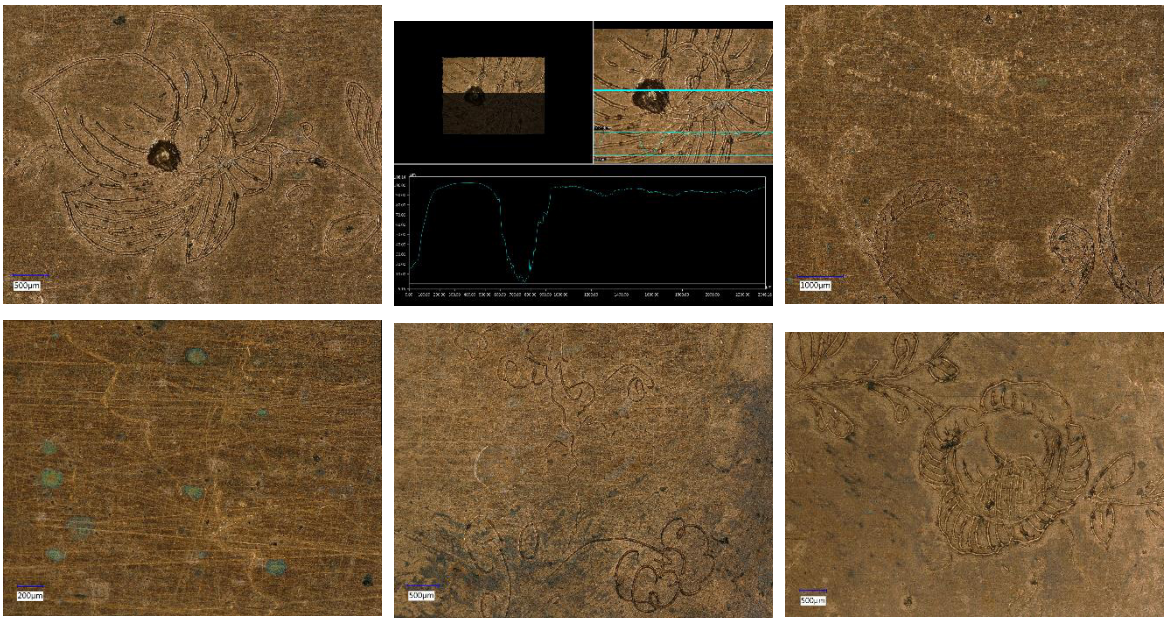
Digitalverweise:

REM, EDX (Zeiss Supra 55 VP, Universität Wien)



Element	Atomic%	Element	Atomic%
C	37,81	C	49,62
O	9,48	O	17,67
Cu	52,71	Cu	32,72

Lichtmikroskopaufnahmen (z-Scans; Keyence, VHX-5000), Universität für Bodenkultur Wien



Inventarnr.: 83939/35 **Alte Inventarnr.:** MdA4, 254

Sammlungsgr.: 530 Metallbearbeitung

akt. Standort: Standorte-TMW/TMW-Museum/E5/3-102

Titel: Galvanoplastisch erzeugtes Medaillon

Hersteller_in: Theyer, Franz; Waidele, Erwin

Ort: Wien

Datierung: 1840 **bis** 1845

Maße:

Breite 4 cm

Tiefe 4.7 cm

Höhe 0.1 cm

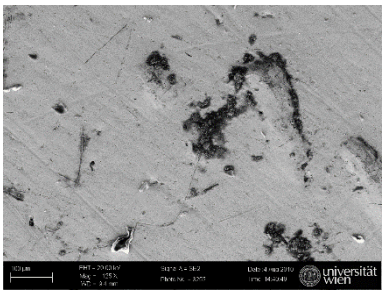
Beschreibung:

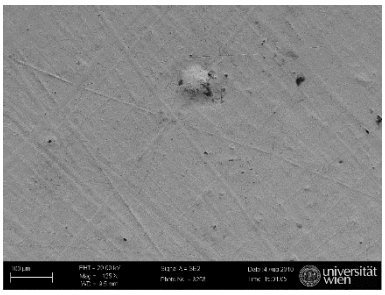
Befindet sich in Lade 2 (von oben gezählt) auf der mit schwarzem Stoff bespannten Tafel. Dort befinden sich lose die Objekte mit den Nummern 254, 258, 259, 260, 261, 262, 263, 266, 267, 269, 270, 271, 275, 289, 290, 293, 295, 296, 299, 300, 301, 303; montiert auf der Tafel sind die Objekte mit den Nummern 264, 265, 278-288, 291, 294, 297. Es fehlen die Objekte mit den Nummern 255, 256, 257, 268, 272, 273, 274, 276, 277, 292, 298, 302 und 304.

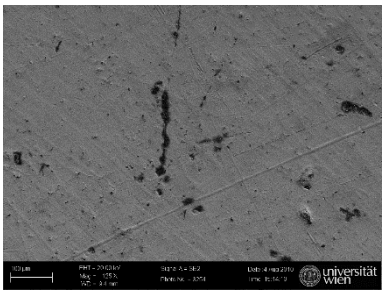
Schlagworte: Kupfer, vergoldet

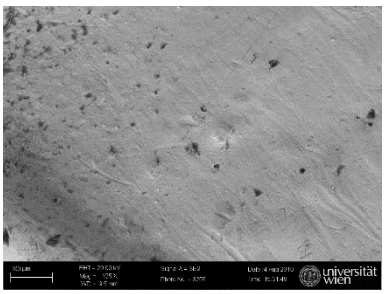
Digitalverweise:

REM, EDX (Zeiss Supra 55 VP, Universität Wien)



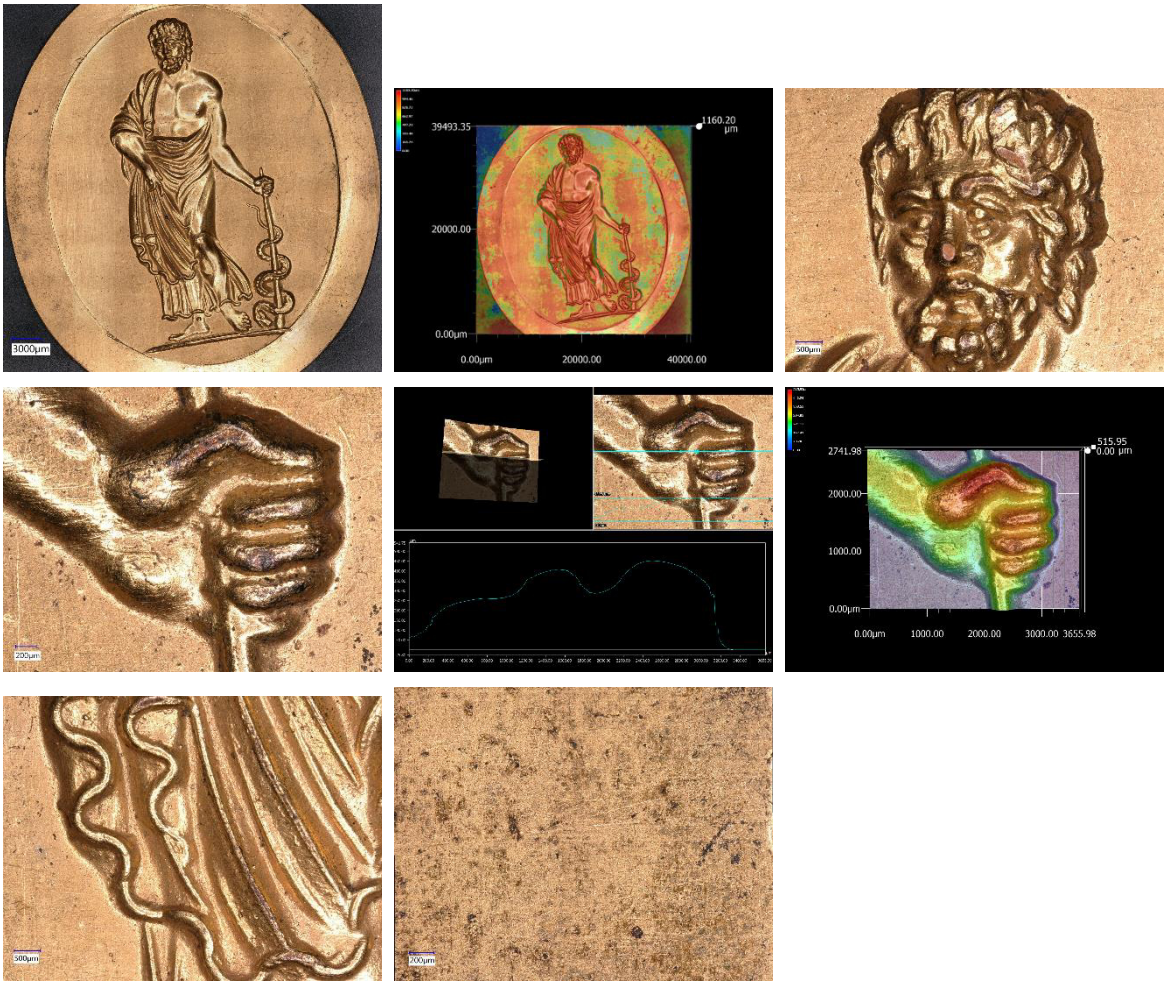






Element	Atomic%	Element	Atomic%	Element	Atomic%	Element	Atomic%
C	71,9	C	58,21	C	64,57	C	57,1
O	18,32	O	19,44	O	13,97	O	26,71
S	3,27	Cu	7,14	Cu	7,2	Ca	0,31
Co	0,22	Au	28,63	Ag	0,69	Cu	4,17
Cu	5,13	Rn	0,31	Au	13,57	Ag	0,37
Ag	0,35					Au	11,34
Au	21,93						

Lichtmikroskopaufnahmen (z-Scans; Keyence, VHX-5000), Universität für Bodenkultur Wien



Inventarnr.: 83939/36 **Alte Inventarnr.:** MdA4, 258

Sammlungsgr.: 530 Metallbearbeitung

akt. Standort: Standorte-TMW/TMW-Museum/E5/3-102

Titel: Galvanoplastisch erzeugtes Medaillon

Hersteller_in: Theyer, Franz; Waidele, Erwin

Ort: Wien

Datierung: 1840 **bis** 1845

Maße:

Breite 6 cm

Tiefe 4.5 cm

Höhe 0.1 cm

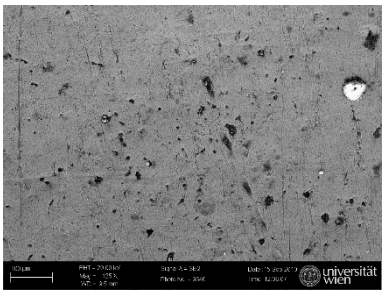
Beschreibung:

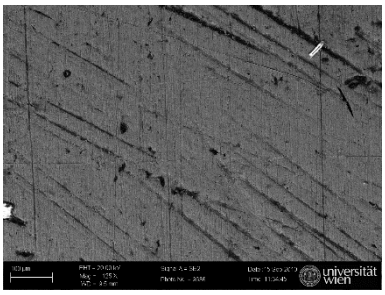
Befindet sich in Lade 2 (von oben gezählt) auf der mit schwarzem Stoff bespannten Tafel. Dort befinden sich lose die Objekte mit den Nummern 254, 258, 259, 260, 261, 262, 263, 266, 267, 269, 270, 271, 275, 289, 290, 293, 295, 296, 299, 300, 301, 303; montiert auf der Tafel sind die Objekte mit den Nummern 264, 265, 278-288, 291, 294, 297. Es fehlen die Objekte mit den Nummern 255, 256, 257, 268, 272, 273, 274, 276, 277, 292, 298, 302 und 304.

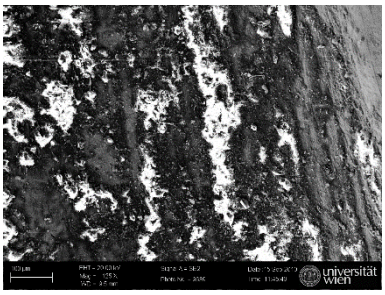
Schlagworte: Kupfer

Digitalverweise:

REM, EDX (Zeiss Supra 55 VP, Universität Wien)

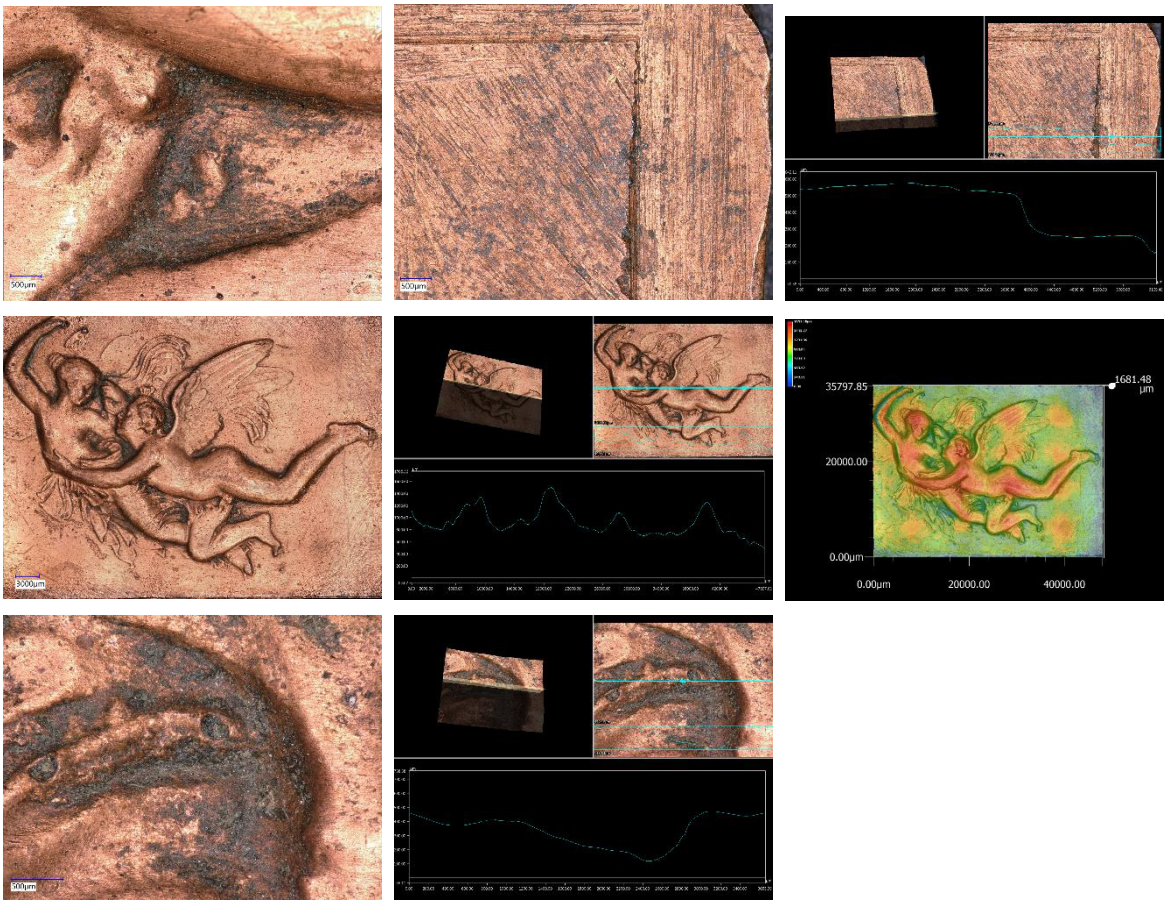






Element	Atomic%	Element	Atomic%	Element	Atomic%
C	59,64	C	58,71	C	56,57
O	14,21	O	27,23	O	16,68
Si	0,37	Mg	0,44	Al	0,33
Cu	25,33	Al	0,89	Si	0,23
Zn	0,45	Si	1,96	S	0,3
		S	0,56	Cu	25,9
		Cl	0,21		
		K	0,24		
		Ca	0,58		
		Cu	9,97		

Lichtmikroskopaufnahmen (z-Scans; Keyence, VHX-5000), Universität für Bodenkultur Wien



Inventarnr.: 83939/37 **Alte Inventarnr.:** MdA4, 259

Sammlungsgr.: 530 Metallbearbeitung

akt. Standort: Standorte-TMW/TMW-Museum/E5/3-102

Titel: Galvanoplastisch erzeugtes Medaillon

Hersteller_in: Theyer, Franz; Waidele, Erwin

Ort: Wien

Datierung: 1840 **bis** 1845

Maße:

Breite 19.2 cm

Tiefe 15.2 cm

Höhe 0.5 cm

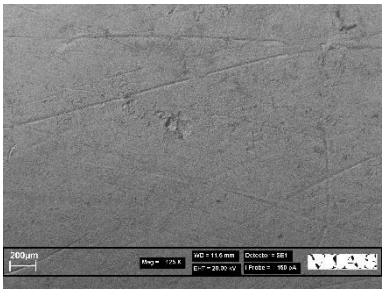
Beschreibung:

Befindet sich in Lade 2 (von oben gezählt) auf der mit schwarzem Stoff bespannten Tafel. Dort befinden sich lose die Objekte mit den Nummern 254, 258, 259, 260, 261, 262, 263, 266, 267, 269, 270, 271, 275, 289, 290, 293, 295, 296, 299, 300, 301, 303; montiert auf der Tafel sind die Objekte mit den Nummern 264, 265, 278-288, 291, 294, 297. Es fehlen die Objekte mit den Nummern 255, 256, 257, 268, 272, 273, 274, 276, 277, 292, 298, 302 und 304.

Schlagworte: Kupfer

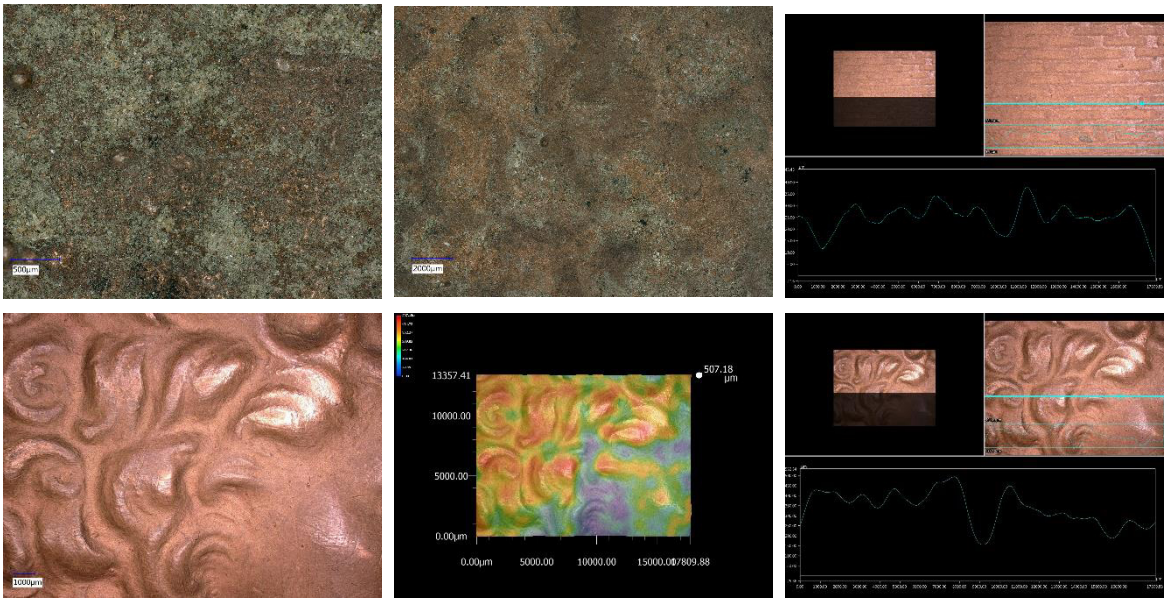
Digitalverweise:

REM, EDX (Zeiss EVO 60 XVP, Universität Wien)



Element	Atomic%
C	55.87
O	19.76
S	0.33
Cu	24.03

Lichtmikroskopaufnahmen (z-Scans; Keyence, VHX-5000), Universität für Bodenkultur Wien



Inventarnr.: 83939/38 **Alte Inventarnr.:** MdA4, 260

Sammlungsgr.: 530 Metallbearbeitung

akt. Standort: Standorte-TMW/TMW-Museum/E5/3-102

Titel: Galvanoplastisch erzeugtes Medaillon

Hersteller_in: Theyer, Franz; Waidele, Erwin

Ort: Wien

Datierung: 1840 **bis** 1845

Maße:

Breite 19.5 cm

Tiefe 15.5 cm

Höhe 0.5 cm

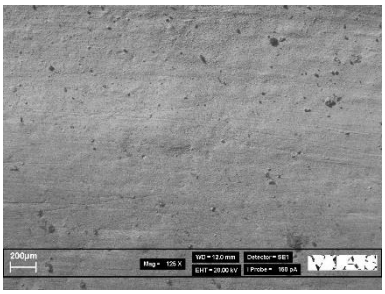
Beschreibung:

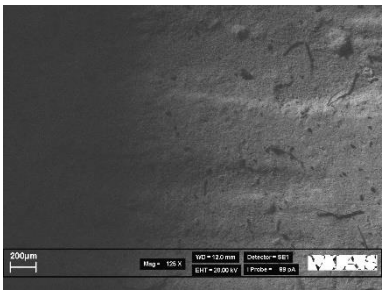
Befindet sich in Lade 2 (von oben gezählt) auf der mit schwarzem Stoff bespannten Tafel. Dort befinden sich lose die Objekte mit den Nummern 254, 258, 259, 260, 261, 262, 263, 266, 267, 269, 270, 271, 275, 289, 290, 293, 295, 296, 299, 300, 301, 303; montiert auf der Tafel sind die Objekte mit den Nummern 264, 265, 278-288, 291, 294, 297. Es fehlen die Objekte mit den Nummern 255, 256, 257, 268, 272, 273, 274, 276, 277, 292, 298, 302 und 304.

Schlagworte: Kupfer

Digitalverweise:

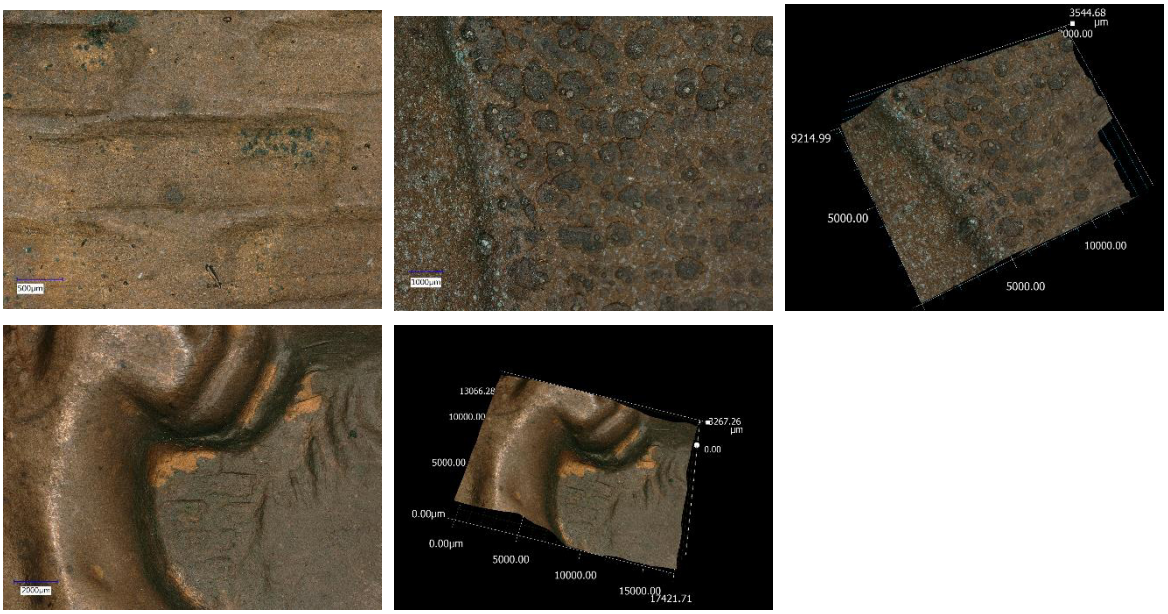
REM, EDX (Zeiss EVO 60 XVP, Universität Wien)





Element	Atomic%
C	57.78
O	16.18
S	0.25
Cu	25.79

Lichtmikroskopaufnahmen (z-Scans; Keyence, VHX-5000), Universität für Bodenkultur Wien



Inventarnr.: 83939/39 **Alte Inventarnr.:** MdA4, 261

Sammlungsgr.: 530 Metallbearbeitung

akt. Standort: Standorte-TMW/TMW-Museum/E5/3-102

Titel: Galvanoplastisch erzeugtes Medaillon

Hersteller_in: Theyer, Franz; Waidele, Erwin

Ort: Wien

Datierung: 1840 **bis** 1845

Maße:

Breite 5.3 cm

Tiefe 4.9 cm

Höhe 0.2 cm

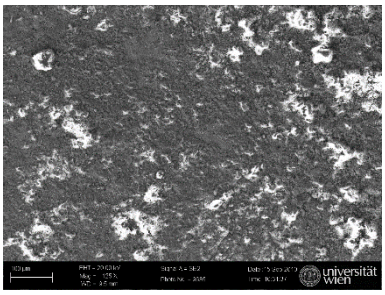
Beschreibung:

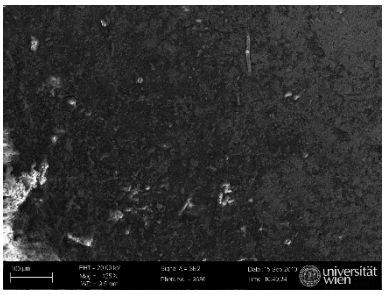
Befindet sich in Lade 2 (von oben gezählt) auf der mit schwarzem Stoff bespannten Tafel. Dort befinden sich lose die Objekte mit den Nummern 254, 258, 259, 260, 261, 262, 263, 266, 267, 269, 270, 271, 275, 289, 290, 293, 295, 296, 299, 300, 301, 303; montiert auf der Tafel sind die Objekte mit den Nummern 264, 265, 278-288, 291, 294, 297. Es fehlen die Objekte mit den Nummern 255, 256, 257, 268, 272, 273, 274, 276, 277, 292, 298, 302 und 304.

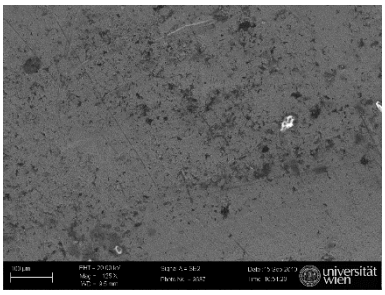
Schlagworte: Kupfer

Digitalverweise:

REM, EDX (Zeiss Supra 55 VP, Universität Wien)







Element	Atomic%	Element	Atomic%	Element	Atomic%
C	34,47	C	63,95	C	61,7
O	44,79	O	27,6	O	15,86
Al	0,36	Al	0,64	S	0,31
Si	0,65	Si	0,91	Cu	22,13
S	2,91	S	0,49		
Cl	0,27	Ca	0,32		
Ca	0,34	Cu	6,1		
Cu	15,96				
Zn	0,24				

Inventarnr.: 83939/40 **Alte Inventarnr.:** MdA4, 262

Sammlungsgr.: 530 Metallbearbeitung

akt. Standort: Standorte-TMW/TMW-Museum/E5/3-102

Titel: Galvanoplastisch erzeugtes Medaillon

Hersteller_in: Theyer, Franz; Waidele, Erwin

Ort: Wien

Datierung: 1840 **bis** 1845

Maße:

Breite 4.9 cm

Tiefe 4.2 cm

Höhe 0.1 cm

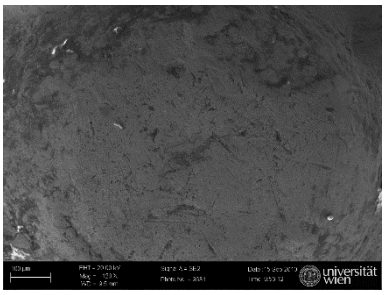
Beschreibung:

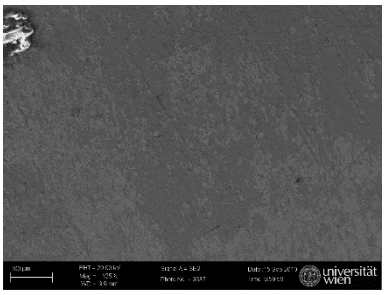
Befindet sich in Lade 2 (von oben gezählt) auf der mit schwarzem Stoff bespannten Tafel. Dort befinden sich lose die Objekte mit den Nummern 254, 258, 259, 260, 261, 262, 263, 266, 267, 269, 270, 271, 275, 289, 290, 293, 295, 296, 299, 300, 301, 303; montiert auf der Tafel sind die Objekte mit den Nummern 264, 265, 278-288, 291, 294, 297. Es fehlen die Objekte mit den Nummern 255, 256, 257, 268, 272, 273, 274, 276, 277, 292, 298, 302 und 304.

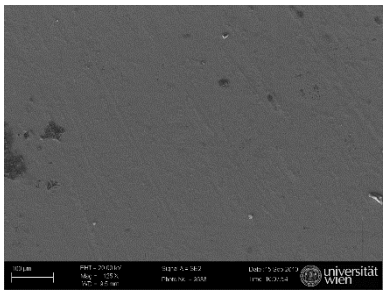
Schlagworte: Kupfer, versilbert

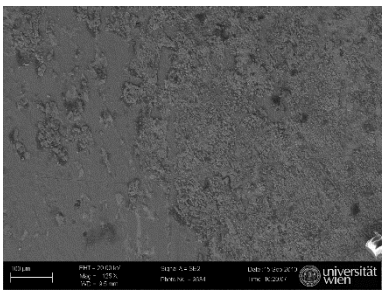
Digitalverweise:

REM, EDX (Zeiss Supra 55 VP, Universität Wien)



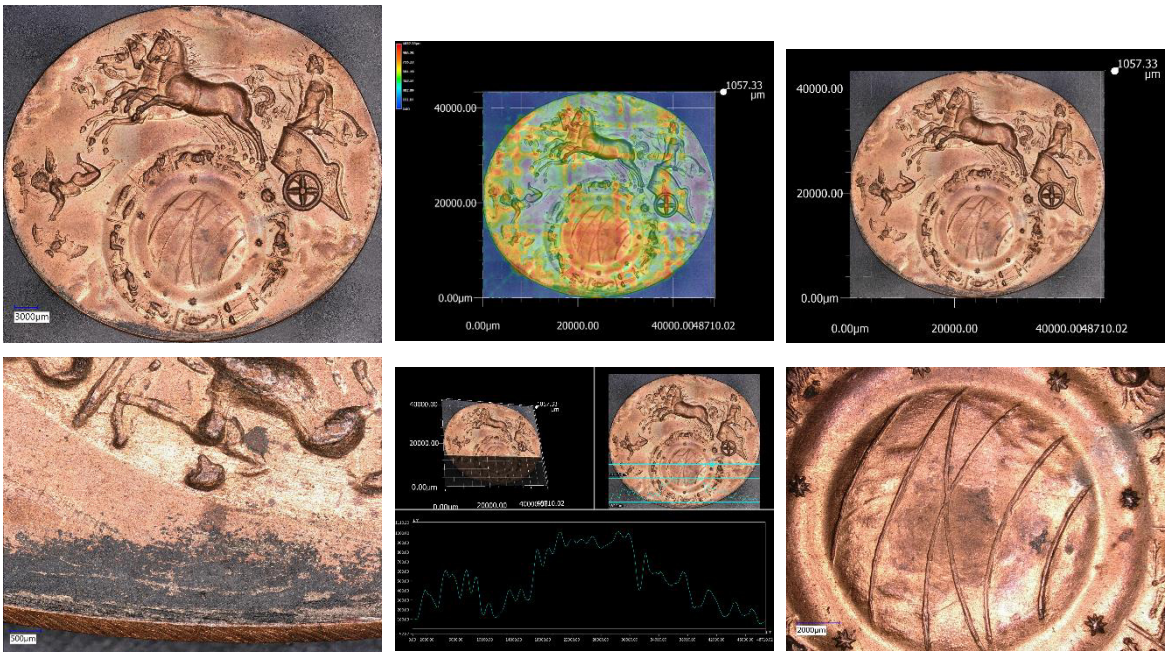






Element	Atomic%	Element	Atomic%	Element	Atomic%	Element	Atomic%
C	64,27	C	47,97	C	50,79	C	55,87
O	20,31	O	18,07	O	10	O	22,66
Al	0,36	Cu	27,81	Cu	39,2	Si	0,25
Si	0,57	Ag	6,16			S	2,13
S	0,9					Ca	0,26
Ca	0,39					Cu	12,64
Cu	12,53					Ag	6,2
Ag	0,66						

Lichtmikroskopaufnahmen (z-Scans; Keyence, VHX-5000), Universität für Bodenkultur Wien



Inventarnr.: 83939/41 **Alte Inventarnr.:** MdA4, 263

Sammlungsgr.: 530 Metallbearbeitung

akt. Standort: Standorte-TMW/TMW-Museum/E5/3-102

Titel: Galvanoplastisch erzeugtes Medaillon

Hersteller_in: Theyer, Franz; Waidele, Erwin

Ort: Wien

Datierung: 1840 **bis** 1845

Maße:

Breite 4.9 cm

Tiefe 6 cm

Höhe 0.1 cm

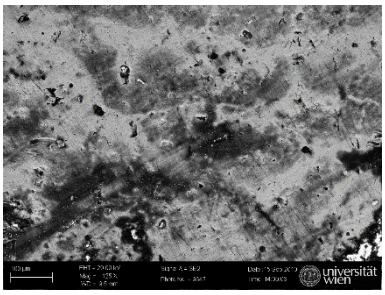
Beschreibung:

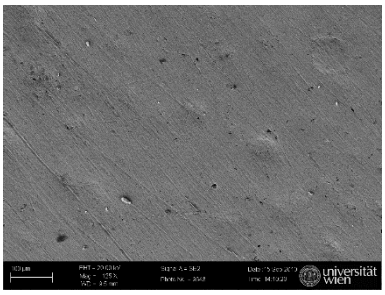
Befindet sich in Lade 2 (von oben gezählt) auf der mit schwarzem Stoff bespannten Tafel. Dort befinden sich lose die Objekte mit den Nummern 254, 258, 259, 260, 261, 262, 263, 266, 267, 269, 270, 271, 275, 289, 290, 293, 295, 296, 299, 300, 301, 303; montiert auf der Tafel sind die Objekte mit den Nummern 264, 265, 278-288, 291, 294, 297. Es fehlen die Objekte mit den Nummern 255, 256, 257, 268, 272, 273, 274, 276, 277, 292, 298, 302 und 304.

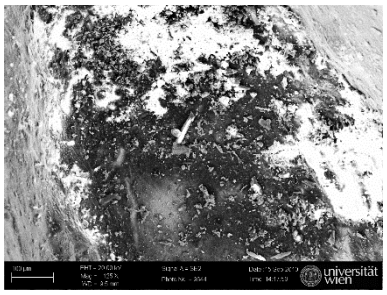
Schlagworte: Kupfer, versilbert

Digitalverweise:

REM, EDX (Zeiss Supra 55 VP, Universität Wien)

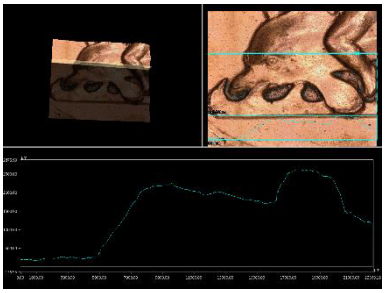






Element	Atomic%	Element	Atomic%	Element	Atomic%
C	76,24	C	56,97	C	71,12
O	8,46	O	9,12	O	21,49
S	0,09	Cu	33,91	Al	0,18
Cl	0,27			Si	0,74
Cu	14,93			S	0,72
				Ca	0,21
				Cu	5,21
				Ag	0,34

Lichtmikroskopaufnahmen (z-Scans; Keyence, VHX-5000), Universität für Bodenkultur Wien



Inventarnr.: 83939/42 **Alte Inventarnr.:** MdA4, 266

Sammlungsgr.: 530 Metallbearbeitung

akt. Standort: Standorte-TMW/TMW-Museum/E5/3-102

Titel: Galvanoplastisch erzeugtes Medaillon

Hersteller_in: Theyer, Franz; Waidele, Erwin

Ort: Wien

Datierung: 1840 **bis** 1845

Maße:

Breite 11.3 cm

Tiefe 7.6 cm

Höhe 0.2 cm

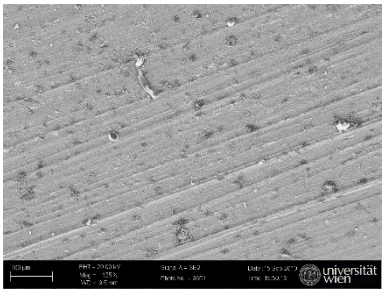
Beschreibung:

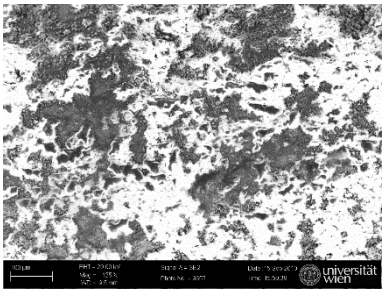
Befindet sich in Lade 2 (von oben gezählt) auf der mit schwarzem Stoff bespannten Tafel. Dort befinden sich lose die Objekte mit den Nummern 254, 258, 259, 260, 261, 262, 263, 266, 267, 269, 270, 271, 275, 289, 290, 293, 295, 296, 299, 300, 301, 303; montiert auf der Tafel sind die Objekte mit den Nummern 264, 265, 278-288, 291, 294, 297. Es fehlen die Objekte mit den Nummern 255, 256, 257, 268, 272, 273, 274, 276, 277, 292, 298, 302 und 304.

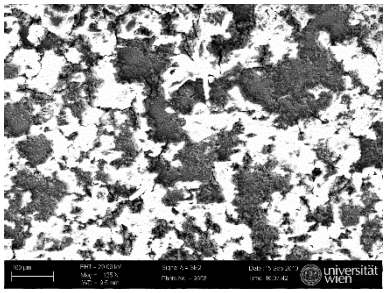
Schlagworte: Kupfer, versilbert

Digitalverweise:

REM, EDX (Zeiss Supra 55 VP, Universität Wien)

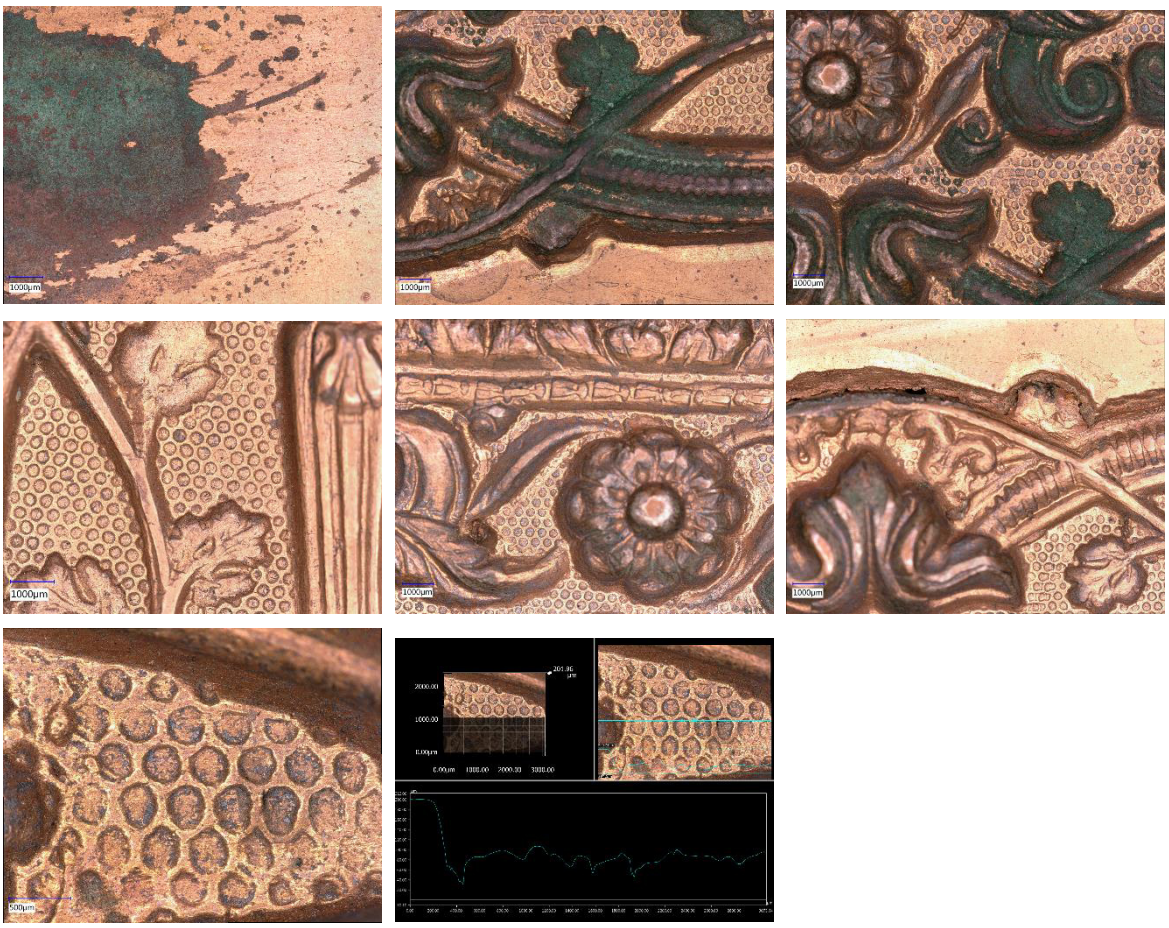






Element	Atomic%	Element	Atomic%	Element	Atomic%
C	55,07	C	53,95	C	36,45
O	16,66	O	33,56	O	46,66
Si	1,11	Al	0,18	Al	0,35
S	0,23	Si	0,47	Si	1,6
Cl	0,29	S	0,7	S	0,69
Cu	25,91	Cl	0,86	Cl	0,89
Ag	0,74	K	0,35	K	0,54
		Ca	0,45	Ca	0,2
		Cu	9,48	Cu	12,62

Lichtmikroskopaufnahmen (z-Scans; Keyence, VHX-5000), Universität für Bodenkultur Wien



Inventarnr.: 83939/43 **Alte Inventarnr.:** MdA4, 267

Sammlungsgr.: 530 Metallbearbeitung

akt. Standort: Standorte-TMW/TMW-Museum/E5/3-102

Titel: Galvanoplastisch erzeugtes Medaillon

Hersteller_in: Theyer, Franz; Waidele, Erwin

Ort: Wien

Datierung: 1840 **bis** 1845

Maße:

Breite 11.1 cm

Tiefe 7.6 cm

Höhe 0.2 cm

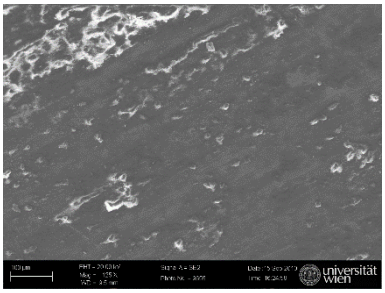
Beschreibung:

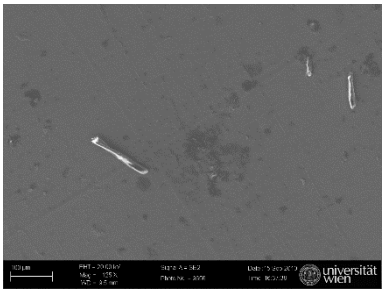
Befindet sich in Lade 2 (von oben gezählt) auf der mit schwarzem Stoff bespannten Tafel. Dort befinden sich lose die Objekte mit den Nummern 254, 258, 259, 260, 261, 262, 263, 266, 267, 269, 270, 271, 275, 289, 290, 293, 295, 296, 299, 300, 301, 303; montiert auf der Tafel sind die Objekte mit den Nummern 264, 265, 278-288, 291, 294, 297. Es fehlen die Objekte mit den Nummern 255, 256, 257, 268, 272, 273, 274, 276, 277, 292, 298, 302 und 304.

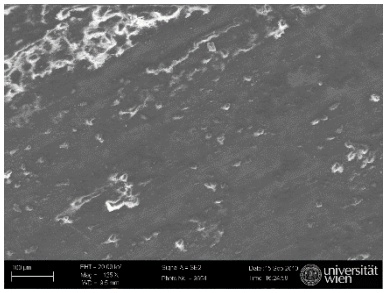
Schlagworte: Kupfer, versilbert

Digitalverweise:

REM, EDX (Zeiss Supra 55 VP, Universität Wien)

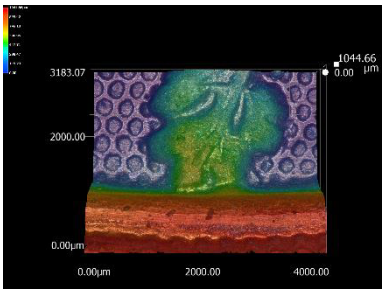


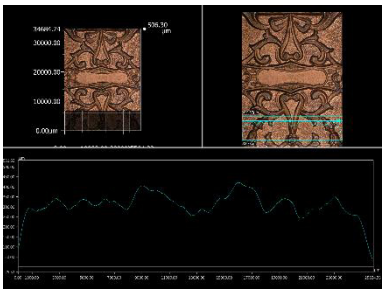


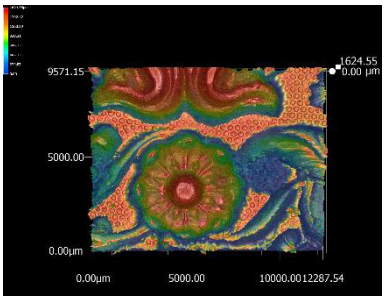


Element	Atomic%	Element	Atomic%
C	53,77	C	62,82
O	33,78	O	16,56
Al	0,27	Si	0,28
Si	0,88	S	0,2
S	0,53	Cu	19,93
K	0,6	Ag	0,21
Ca	0,66		
Cu	9,37		
Ag	0,14		

Lichtmikroskopaufnahmen (z-Scans; Keyence, VHX-5000), Universität für Bodenkultur Wien







Inventarnr.: 83939/44 **Alte Inventarnr.:** MdA4, 269

Sammlungsgr.: 530 Metallbearbeitung

akt. Standort: Standorte-TMW/TMW-Museum/E5/3-102

Titel: Galvanoplastisch erzeugtes Medaillon

Hersteller_in: Theyer, Franz; Waidele, Erwin

Ort: Wien

Datierung: 1840 **bis** 1845

Maße:

Breite 5.7 cm

Tiefe 4.7 cm

Höhe 0.1 cm

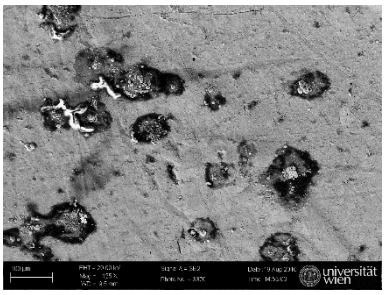
Beschreibung:

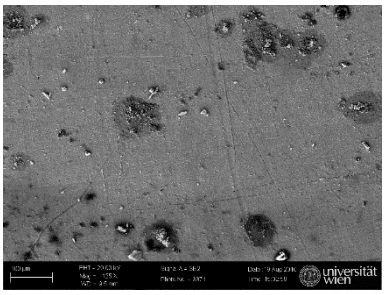
Befindet sich in Lade 2 (von oben gezählt) auf der mit schwarzem Stoff bespannten Tafel. Dort befinden sich lose die Objekte mit den Nummern 254, 258, 259, 260, 261, 262, 263, 266, 267, 269, 270, 271, 275, 289, 290, 293, 295, 296, 299, 300, 301, 303; montiert auf der Tafel sind die Objekte mit den Nummern 264, 265, 278-288, 291, 294, 297. Es fehlen die Objekte mit den Nummern 255, 256, 257, 268, 272, 273, 274, 276, 277, 292, 298, 302 und 304.

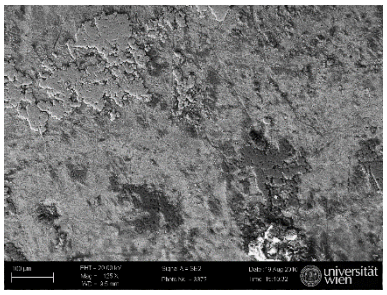
Schlagworte: Kupfer, versilbert

Digitalverweise:

REM, EDX (Zeiss Supra 55 VP, Universität Wien)

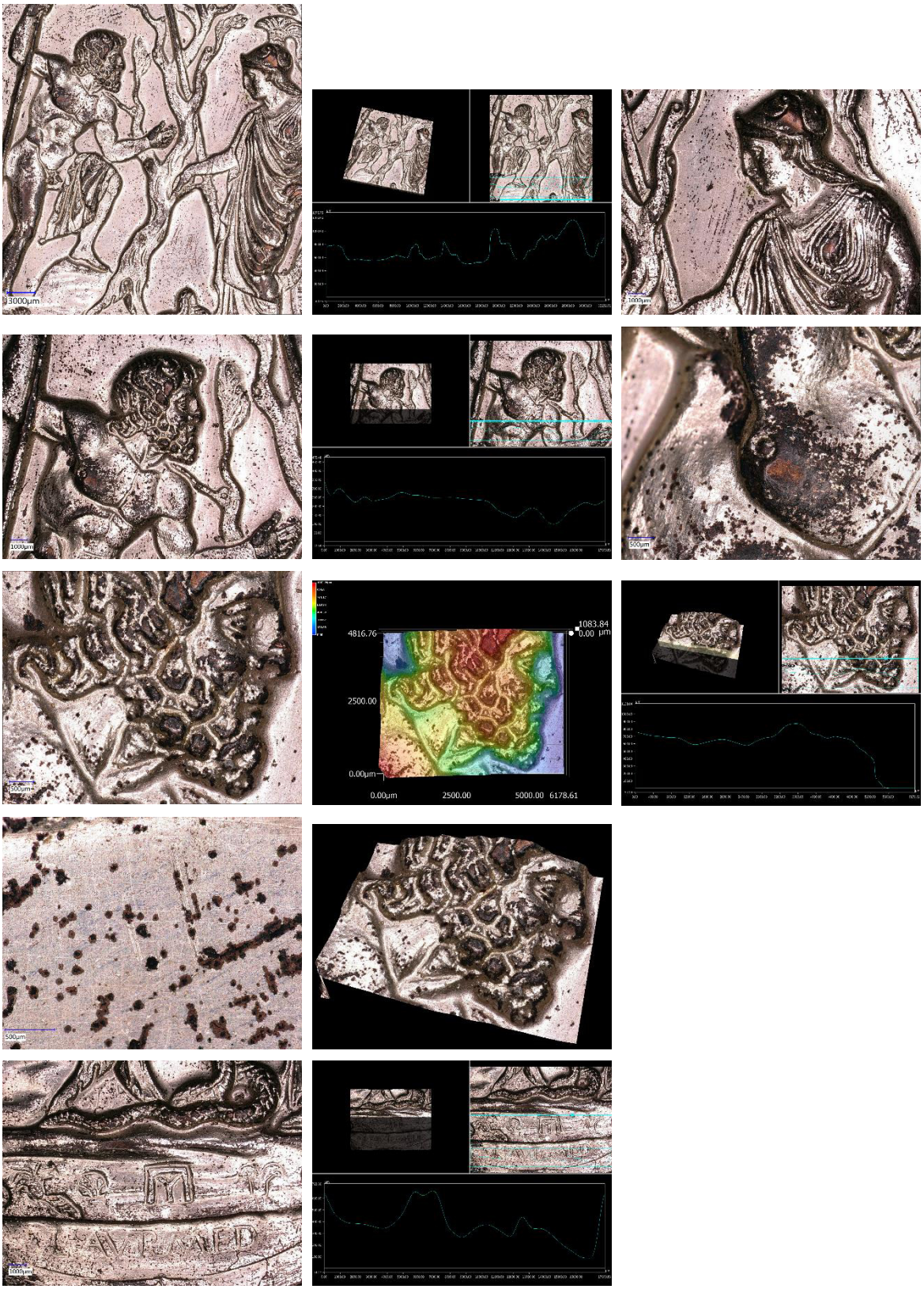






Element	Atomic%	Element	Atomic%	Element	Atomic%
C	63,89	C	52,68	C	64,85
O	22,04	O	21,12	O	16,28
S	0,76	S	1,58	S	4,32
Cu	8,57	Cu	20,96	Cl	0,43
Ag	4,74	Ag	3,66	Cu	13,35
				Ag	0,76

Lichtmikroskopaufnahmen (z-Scans; Keyence, VHX-5000), Universität für Bodenkultur Wien



Inventarnr.: 83939/45 **Alte Inventarnr.:** MdA4, 270

Sammlungsgr.: 530 Metallbearbeitung

akt. Standort: Standorte-TMW/TMW-Museum/E5/3-102

Titel: Galvanoplastisch erzeugtes Medaillon

Hersteller_in: Theyer, Franz; Waidele, Erwin

Ort: Wien

Datierung: 1840 **bis** 1845

Maße:

Breite 9.1 cm

Tiefe 12.5 cm

Höhe 1 cm

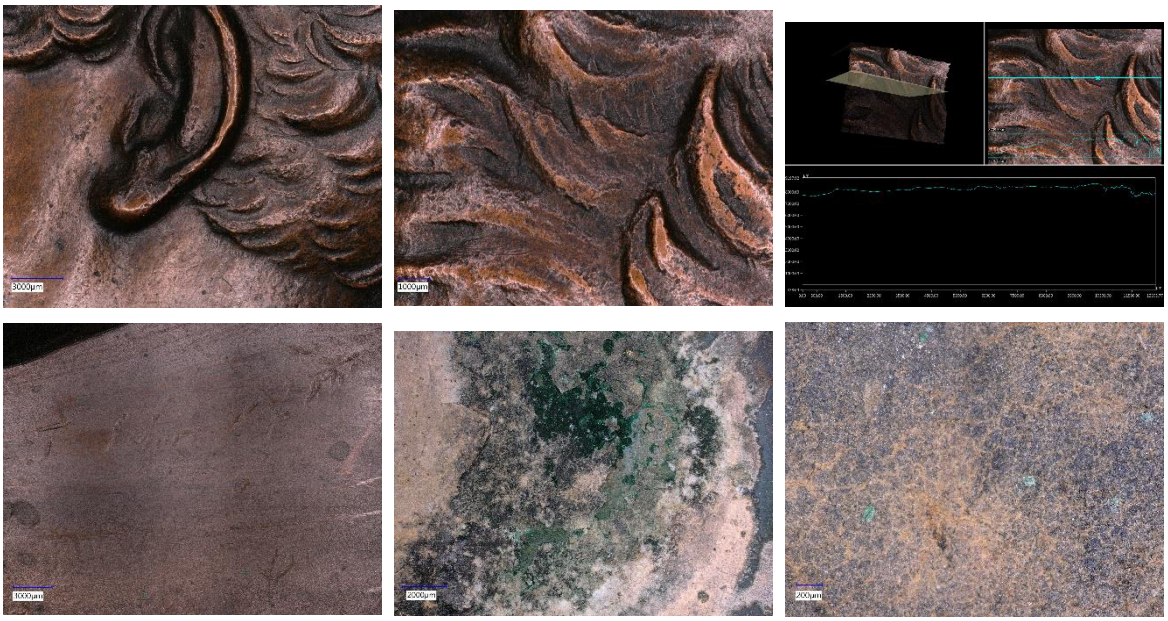
Beschreibung:

Befindet sich in Lade 2 (von oben gezählt) auf der mit schwarzem Stoff bespannten Tafel. Dort befinden sich lose die Objekte mit den Nummern 254, 258, 259, 260, 261, 262, 263, 266, 267, 269, 270, 271, 275, 289, 290, 293, 295, 296, 299, 300, 301, 303; montiert auf der Tafel sind die Objekte mit den Nummern 264, 265, 278-288, 291, 294, 297. Es fehlen die Objekte mit den Nummern 255, 256, 257, 268, 272, 273, 274, 276, 277, 292, 298, 302 und 304.

Schlagworte: Kupfer, versilbert

Digitalverweise:

Lichtmikroskopaufnahmen (z-Scans; Keyence, VHX-5000), Universität für Bodenkultur Wien



Inventarnr.: 83939/46 **Alte Inventarnr.:** MdA4, 271

Sammlungsgr.: 530 Metallbearbeitung

akt. Standort: Standorte-TMW/TMW-Museum/E5/3-102

Titel: Galvanoplastisch erzeugtes Medaillon

Hersteller_in: Theyer, Franz; Waidele, Erwin

Ort: Wien

Datierung: 1840 **bis** 1845

Maße:

Breite 5.5 cm

Tiefe 8.2 cm

Höhe 0.1 cm

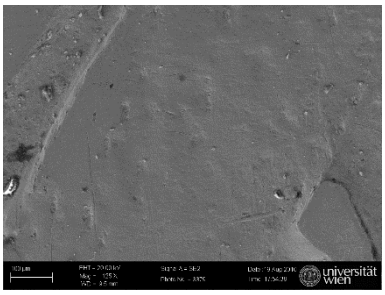
Beschreibung:

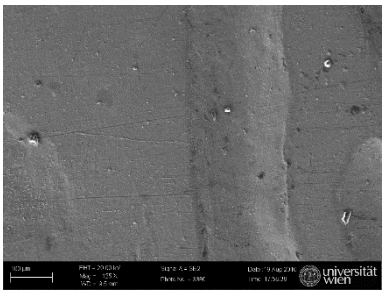
Befindet sich in Lade 2 (von oben gezählt) auf der mit schwarzem Stoff bespannten Tafel. Dort befinden sich lose die Objekte mit den Nummern 254, 258, 259, 260, 261, 262, 263, 266, 267, 269, 270, 271, 275, 289, 290, 293, 295, 296, 299, 300, 301, 303; montiert auf der Tafel sind die Objekte mit den Nummern 264, 265, 278-288, 291, 294, 297. Es fehlen die Objekte mit den Nummern 255, 256, 257, 268, 272, 273, 274, 276, 277, 292, 298, 302 und 304.

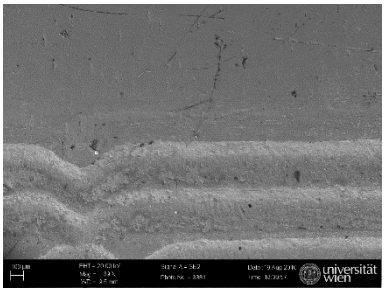
Schlagworte: Kupfer, versilbert, vergoldet

Digitalverweise:

REM, EDX (Zeiss Supra 55 VP, Universität Wien)

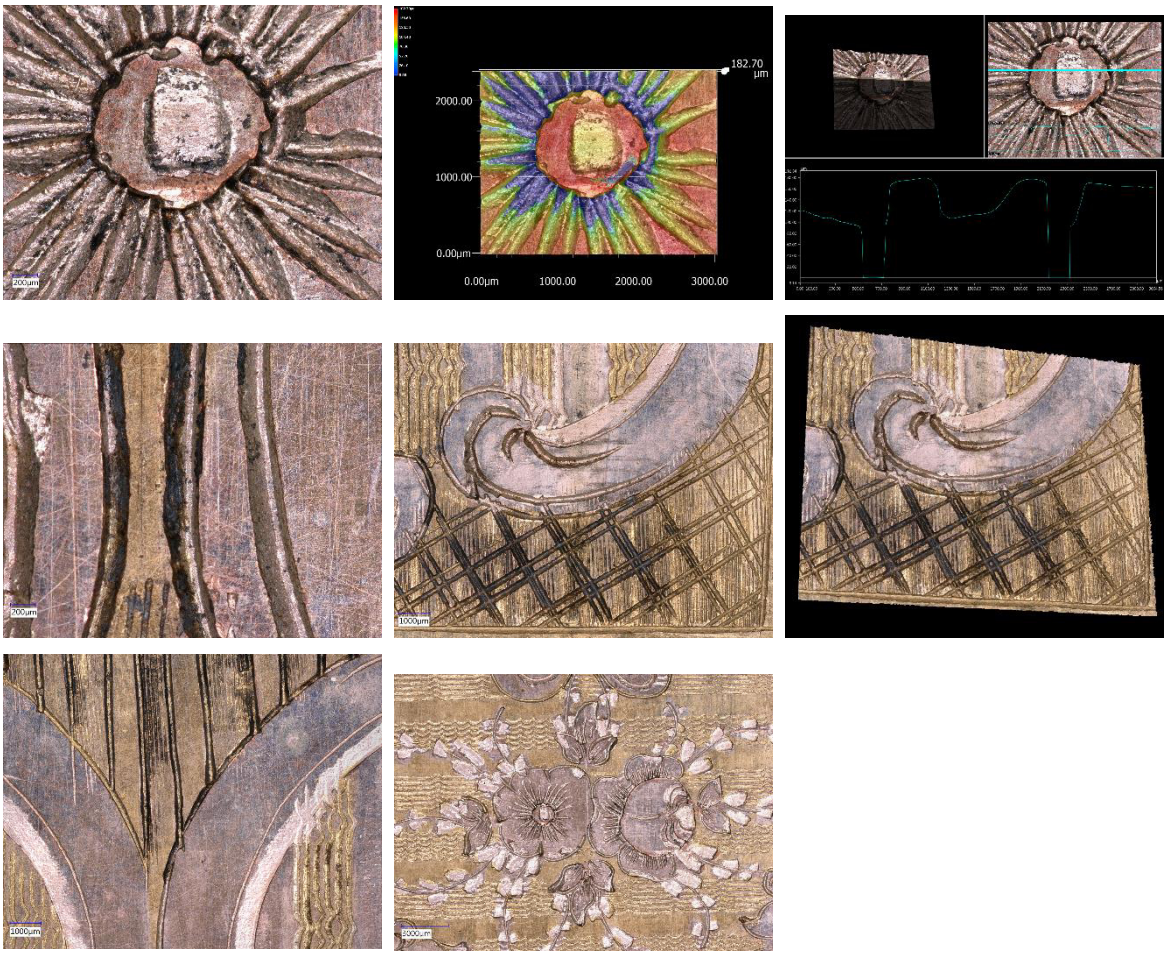






Element	Atomic%	Element	Atomic%	Element	Atomic%	Element	Atomic%
C	71,37	C	52,17	C	55,75	C	52,49
O	13,97	O	17,75	O	18,23	O	18,72
S	2,46	Cu	25,81	Cu	18,82	S	1,5
Cl	1,36	Ag	4,26	Ag	4,09	Cu	21,74
Cu	8,38			Au	3,11	Ag	4,39
Ag	2,46					Au	1,17

Lichtmikroskopaufnahmen (z-Scans; Keyence, VHX-5000), Universität für Bodenkultur Wien



Inventarnr.: 83939/47 **Alte Inventarnr.:** MdA4, 275

Sammlungsgr.: 530 Metallbearbeitung

akt. Standort: Standorte-TMW/TMW-Museum/E5/3-102

Titel: Galvanoplastisch erzeugtes Medaillon

Hersteller_in: Theyer, Franz; Waidele, Erwin

Ort: Wien

Datierung: 1840 **bis** 1845

Maße:

Breite 5.1 cm

Tiefe 6.1 cm

Höhe 0.3 cm

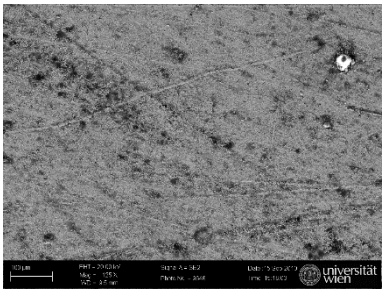
Beschreibung:

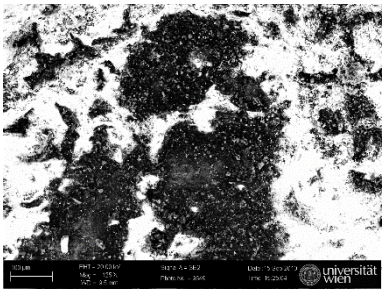
Befindet sich in Lade 2 (von oben gezählt) auf der mit schwarzem Stoff bespannten Tafel. Dort befinden sich lose die Objekte mit den Nummern 254, 258, 259, 260, 261, 262, 263, 266, 267, 269, 270, 271, 275, 289, 290, 293, 295, 296, 299, 300, 301, 303; montiert auf der Tafel sind die Objekte mit den Nummern 264, 265, 278-288, 291, 294, 297. Es fehlen die Objekte mit den Nummern 255, 256, 257, 268, 272, 273, 274, 276, 277, 292, 298, 302 und 304.

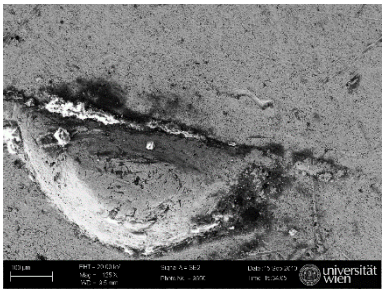
Schlagworte: Kupfer

Digitalverweise:

REM, EDX (Zeiss Supra 55 VP, Universität Wien)

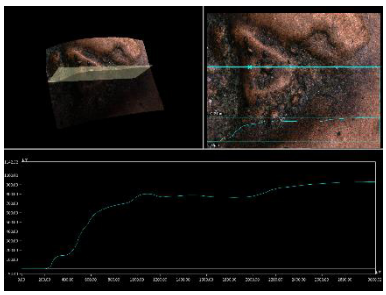


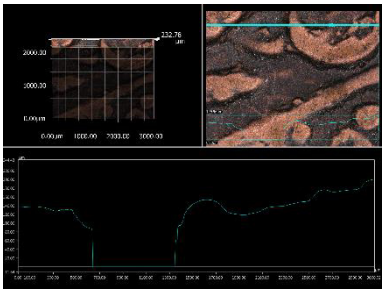




Element	Atomic%	Element	Atomic%	Element	Atomic%
C	73,39	C	68,69	C	63,72
O	11,44	O	28,49	O	11,92
Si	0,41	Al	0,22	Si	0,48
S	0,16	Si	0,68	Cu	23,88
Cu	14,6	S	0,6		
		Ca	0,36		
		Cu	0,97		

Lichtmikroskopaufnahmen (z-Scans; Keyence, VHX-5000), Universität für Bodenkultur Wien





Inventarnr.: 83939/48 **Alte Inventarnr.:** MdA4, 289

Sammlungsgr.: 530 Metallbearbeitung

akt. Standort: Standorte-TMW/TMW-Museum/E5/3-102

Titel: Galvanoplastisch erzeugtes Medaillon

Hersteller_in: Theyer, Franz; Waidele, Erwin

Ort: Wien

Datierung: 1840 **bis** 1845

Maße:

Breite 9.2 cm

Tiefe 6 cm

Höhe 0.3 cm

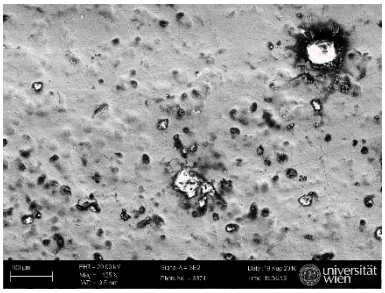
Beschreibung:

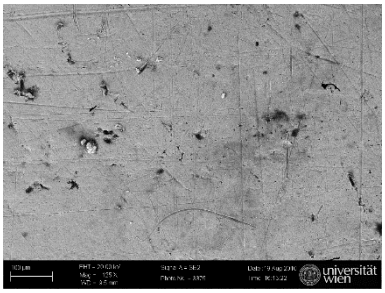
Befindet sich in Lade 2 (von oben gezählt) auf der mit schwarzem Stoff bespannten Tafel. Dort befinden sich lose die Objekte mit den Nummern 254, 258, 259, 260, 261, 262, 263, 266, 267, 269, 270, 271, 275, 289, 290, 293, 295, 296, 299, 300, 301, 303; montiert auf der Tafel sind die Objekte mit den Nummern 264, 265, 278-288, 291, 294, 297. Es fehlen die Objekte mit den Nummern 255, 256, 257, 268, 272, 273, 274, 276, 277, 292, 298, 302 und 304.

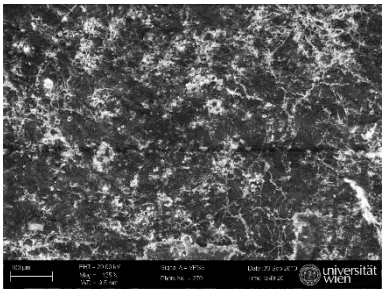
Schlagworte: Kupfer

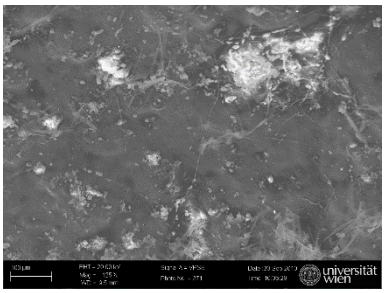
Digitalverweise:

REM, EDX (Zeiss Supra 55 VP, Universität Wien)



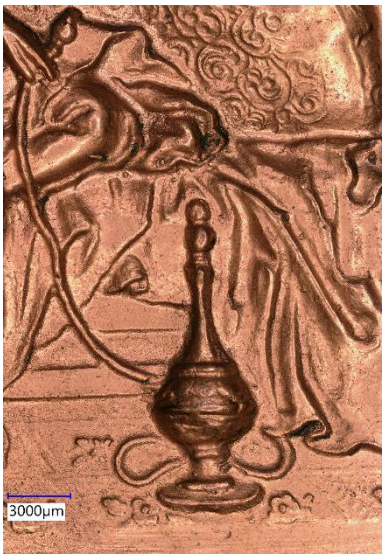






Element	Atomic%	Element	Atomic%	Element	Atomic%	Element	Atomic%
C	76,52	C	81,66	C	76,82	C	75,24
O	22,42	O	17,84	O	12,58	O	38,27
Si	0,16	S	0,37	Si	0,12	Mg	0,33
S	0,38	Cu	0,13	S	0,19	Si	0,19
Ca	0,09			Ca	0,08	S	0,39
Cu	0,44			Cu	10,22	K	0,12
						Ca	0,32
						Cu	5,52

Lichtmikroskopaufnahmen (z-Scans; Keyence, VHX-5000), Universität für Bodenkultur Wien



Inventarnr.: 83939/49 **Alte Inventarnr.:** MdA4, 290

Sammlungsgr.: 530 Metallbearbeitung

akt. Standort: Standorte-TMW/TMW-Museum/E5/3-102

Titel: Galvanoplastisch erzeugtes Medaillon

Hersteller_in: Theyer, Franz; Waidele, Erwin

Ort: Wien

Datierung: 1840 **bis** 1845

Maße:

Breite 9.1 cm

Tiefe 6 cm

Höhe 0.1 cm

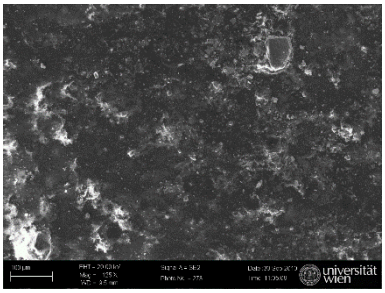
Beschreibung:

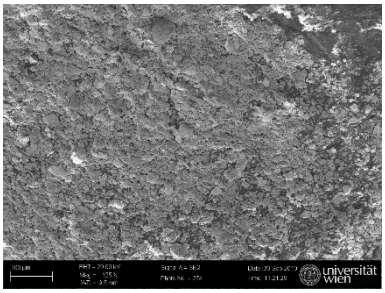
Befindet sich in Lade 2 (von oben gezählt) auf der mit schwarzem Stoff bespannten Tafel. Dort befinden sich lose die Objekte mit den Nummern 254, 258, 259, 260, 261, 262, 263, 266, 267, 269, 270, 271, 275, 289, 290, 293, 295, 296, 299, 300, 301, 303; montiert auf der Tafel sind die Objekte mit den Nummern 264, 265, 278-288, 291, 294, 297. Es fehlen die Objekte mit den Nummern 255, 256, 257, 268, 272, 273, 274, 276, 277, 292, 298, 302 und 304.

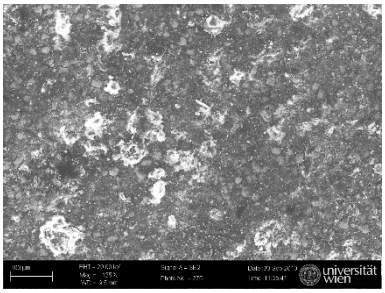
Schlagworte: Kupfer

Digitalverweise:

REM, EDX (Zeiss Supra 55 VP, Universität Wien)

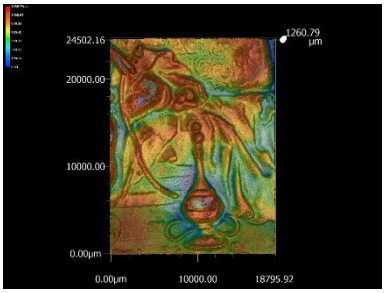


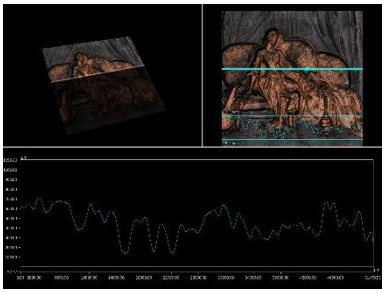


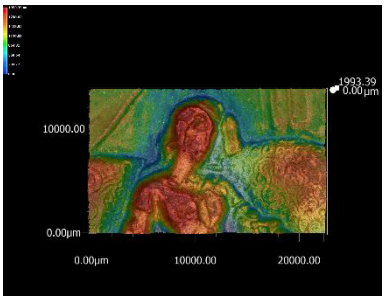


Element	Atomic%	Element	Atomic%	Element	Atomic%
C	69,38	C	64,5	O	69,6
O	26,73	O	19,13	Si	1,1
Si	0,14	S	0,19	S	3,38
S	0,57	Cl	0,19	Cl	10,76
Cl	1,12	Ca	0,32	Ca	0,66
Ca	0,11	Cu	14,03	Ti	0,57
Ti	0,1	Sn	1,65	Fe	0,89
Fe	0,11			Cu	13,05
Cu	1,73				69,6

Lichtmikroskopaufnahmen (z-Scans; Keyence, VHX-5000), Universität für Bodenkultur Wien







Inventarnr.: 83939/50 **Alte Inventarnr.:** MdA4, 293

Sammlungsgr.: 530 Metallbearbeitung

akt. Standort: Standorte-TMW/TMW-Museum/E5/3-102

Titel: Galvanoplastisch erzeugtes Medaillon

Hersteller_in: Theyer, Franz; Waidele, Erwin

Ort: Wien

Datierung: 1840 **bis** 1845

Maße:

Breite 6 cm

Tiefe 4 cm

Höhe 0.1 cm

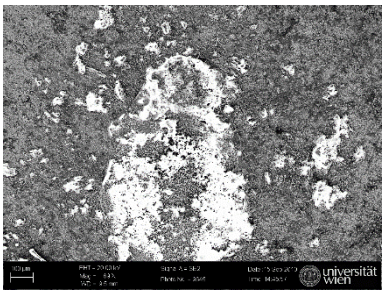
Beschreibung:

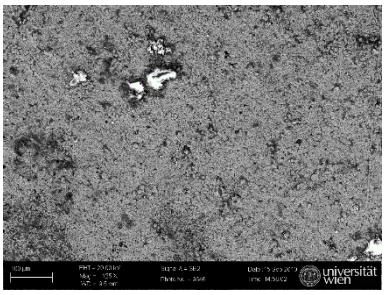
Befindet sich in Lade 2 (von oben gezählt) auf der mit schwarzem Stoff bespannten Tafel. Dort befinden sich lose die Objekte mit den Nummern 254, 258, 259, 260, 261, 262, 263, 266, 267, 269, 270, 271, 275, 289, 290, 293, 295, 296, 299, 300, 301, 303; montiert auf der Tafel sind die Objekte mit den Nummern 264, 265, 278-288, 291, 294, 297. Es fehlen die Objekte mit den Nummern 255, 256, 257, 268, 272, 273, 274, 276, 277, 292, 298, 302 und 304.

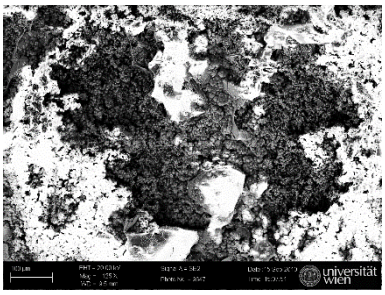
Schlagworte: Kupfer

Digitalverweise:

REM, EDX (Zeiss Supra 55 VP, Universität Wien)

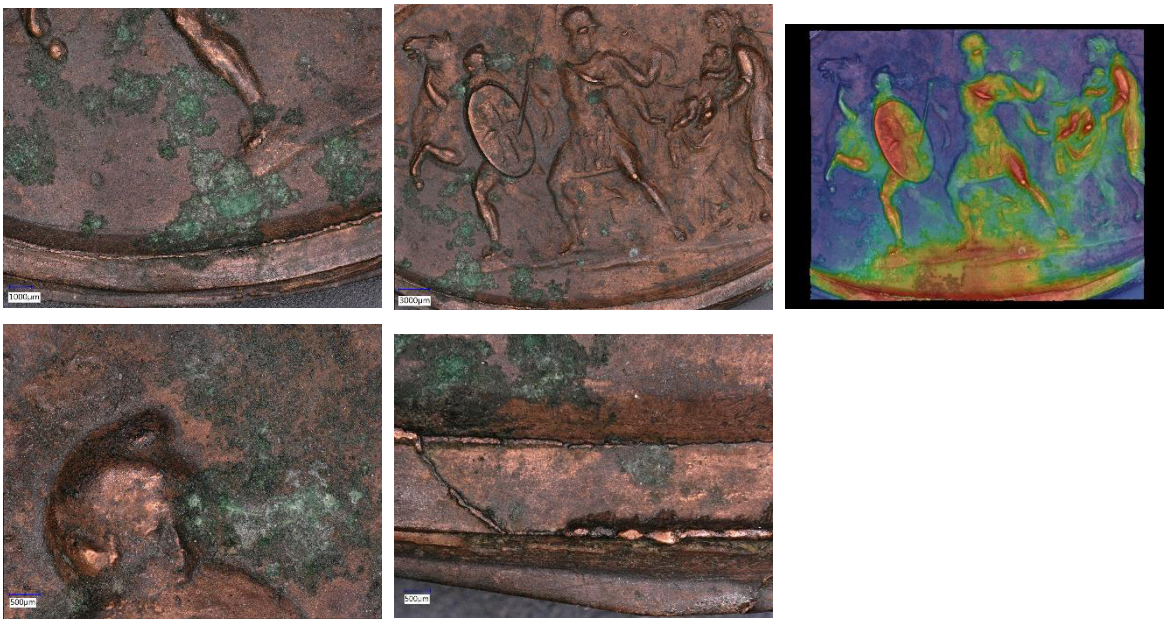






Element	Atomic%	Element	Atomic%	Element	Atomic%
C	36,1	C	64,94	C	44,82
O	45,37	O	13,15	O	45,92
Si	0,63	Si	0,2	Si	0,25
S	2,06	S	0,18	S	0,8
Cl	1,17	Cu	21,54	Cl	2,91
Ca	0,05			Cu	5,3
Fe	0,21				
Cu	13,13				
Zn	1,28				

Lichtmikroskopaufnahmen (z-Scans; Keyence, VHX-5000), Universität für Bodenkultur Wien



Inventarnr.: 83939/51 **Alte Inventarnr.:** MdA4, 295

Sammlungsgr.: 530 Metallbearbeitung

akt. Standort: Standorte-TMW/TMW-Museum/E5/3-102

Titel: Galvanoplastisch erzeugtes Medaillon

Hersteller_in: Theyer, Franz; Waidele, Erwin

Ort: Wien

Datierung: 1840 **bis** 1845

Maße:

Breite 9 cm

Tiefe 5.8 cm

Höhe 0.3 cm

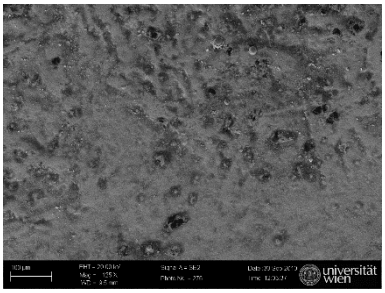
Beschreibung:

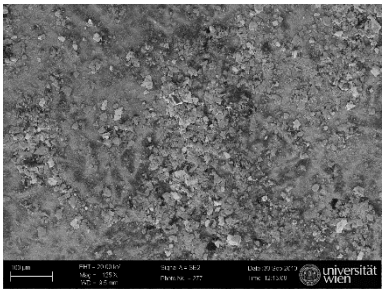
Befindet sich in Lade 2 (von oben gezählt) auf der mit schwarzem Stoff bespannten Tafel. Dort befinden sich lose die Objekte mit den Nummern 254, 258, 259, 260, 261, 262, 263, 266, 267, 269, 270, 271, 275, 289, 290, 293, 295, 296, 299, 300, 301, 303; montiert auf der Tafel sind die Objekte mit den Nummern 264, 265, 278-288, 291, 294, 297. Es fehlen die Objekte mit den Nummern 255, 256, 257, 268, 272, 273, 274, 276, 277, 292, 298, 302 und 304.

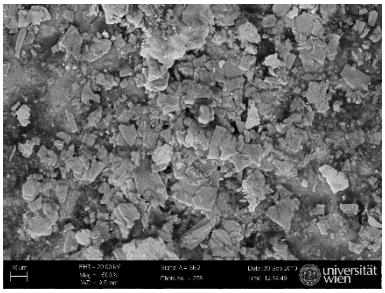
Schlagworte: Kupfer

Digitalverweise:

REM, EDX (Zeiss Supra 55 VP, Universität Wien)

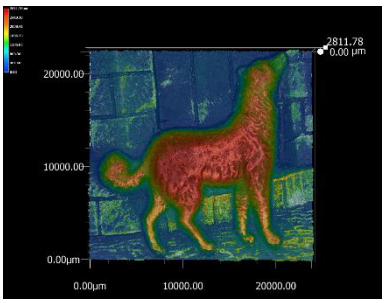


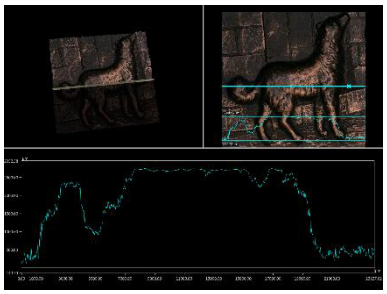




Element	Atomic%	Element	Atomic%
C	57,55	C	55,54
O	22,62	O	24,96
Al	0,26	Al	0,39
Si	0,3	Si	0,78
S	1,87	S	1,24
Cl	0,25	Ca	0,54
Ca	0,29	Fe	0,55
Fe	0,76	Cu	14,17
Cu	16,09	Sn	1,83

Lichtmikroskopaufnahmen (z-Scans; Keyence, VHX-5000), Universität für Bodenkultur Wien





Inventarnr.: 83939/52 **Alte Inventarnr.:** MdA4, 296

Sammlungsgr.: 530 Metallbearbeitung

akt. Standort: Standorte-TMW/TMW-Museum/E5/3-102

Titel: Galvanoplastisch erzeugtes Medaillon

Hersteller_in: Theyer, Franz; Waidele, Erwin

Ort: Wien

Datierung: 1840 **bis** 1845

Maße:

Breite 8.9 cm

Tiefe 5.6 cm

Höhe 0.2 cm

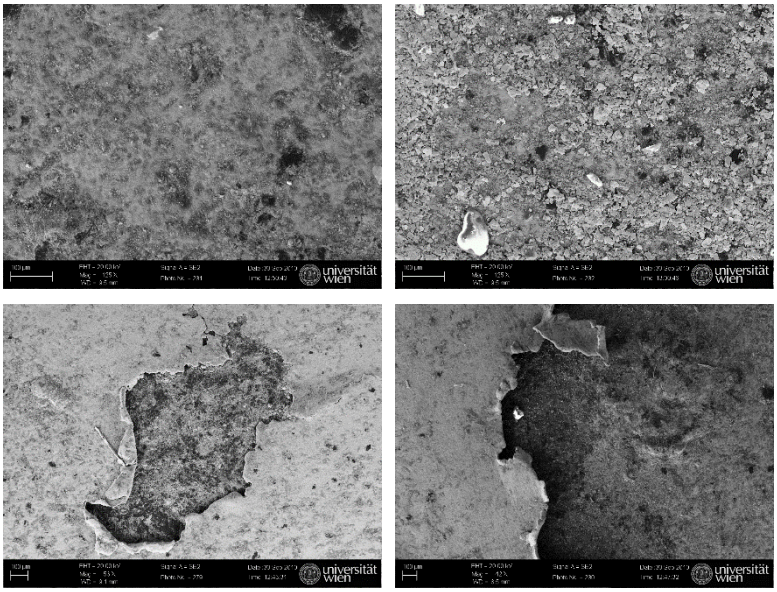
Beschreibung:

Befindet sich in Lade 2 (von oben gezählt) auf der mit schwarzem Stoff bespannten Tafel. Dort befinden sich lose die Objekte mit den Nummern 254, 258, 259, 260, 261, 262, 263, 266, 267, 269, 270, 271, 275, 289, 290, 293, 295, 296, 299, 300, 301, 303; montiert auf der Tafel sind die Objekte mit den Nummern 264, 265, 278-288, 291, 294, 297. Es fehlen die Objekte mit den Nummern 255, 256, 257, 268, 272, 273, 274, 276, 277, 292, 298, 302 und 304.

Schlagworte: Kupfer

Digitalverweise:

REM, EDX (Zeiss Supra 55 VP, Universität Wien)



Element	Atomic%	Element	Atomic%
C	64,21	C	61,67
O	19,78	O	21,37
Al	0,23	Al	0,15
Si	0,32	Si	0,25
S	2	S	1,16
Ca	0,5	Ca	0,38
Fe	0,93	Fe	0,55
Cu	12,03	Cu	12,77
		Sn	1,7

Lichtmikroskopaufnahmen (z-Scans; Keyence, VHX-5000), Universität für Bodenkultur Wien

Inventarnr.: 83939/53 **Alte Inventarnr.:** MdA4, 299

Sammlungsgr.: 530 Metallbearbeitung

akt. Standort: Standorte-TMW/TMW-Museum/E5/3-102

Titel: Galvanoplastisch erzeugter Löffel

Hersteller_in: Theyer, Franz; Waidele, Erwin

Ort: Wien

Datierung: 1840 **bis** 1845

Maße:

Breite 13.1 cm

Tiefe 3.2 cm

Höhe 0.5 cm

Beschreibung:

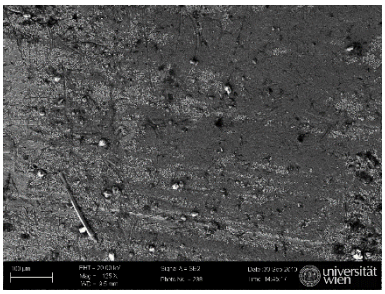
Befindet sich in Lade 2 (von oben gezählt) auf der mit schwarzem Stoff bespannten Tafel. Dort befinden sich lose die Objekte mit den Nummern 254, 258, 259, 260, 261, 262, 263, 266, 267, 269, 270, 271, 275, 289, 290, 293, 295, 296, 299, 300, 301, 303; montiert auf der Tafel sind die Objekte mit den Nummern 264, 265, 278-288, 291, 294, 297. Es fehlen die Objekte mit den Nummern 255, 256, 257, 268, 272, 273, 274, 276, 277, 292, 298, 302 und 304.

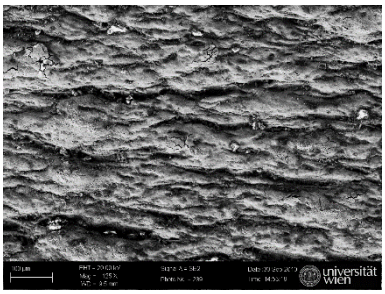
Schlagworte: Messing, versilbert

Digitalverweise:

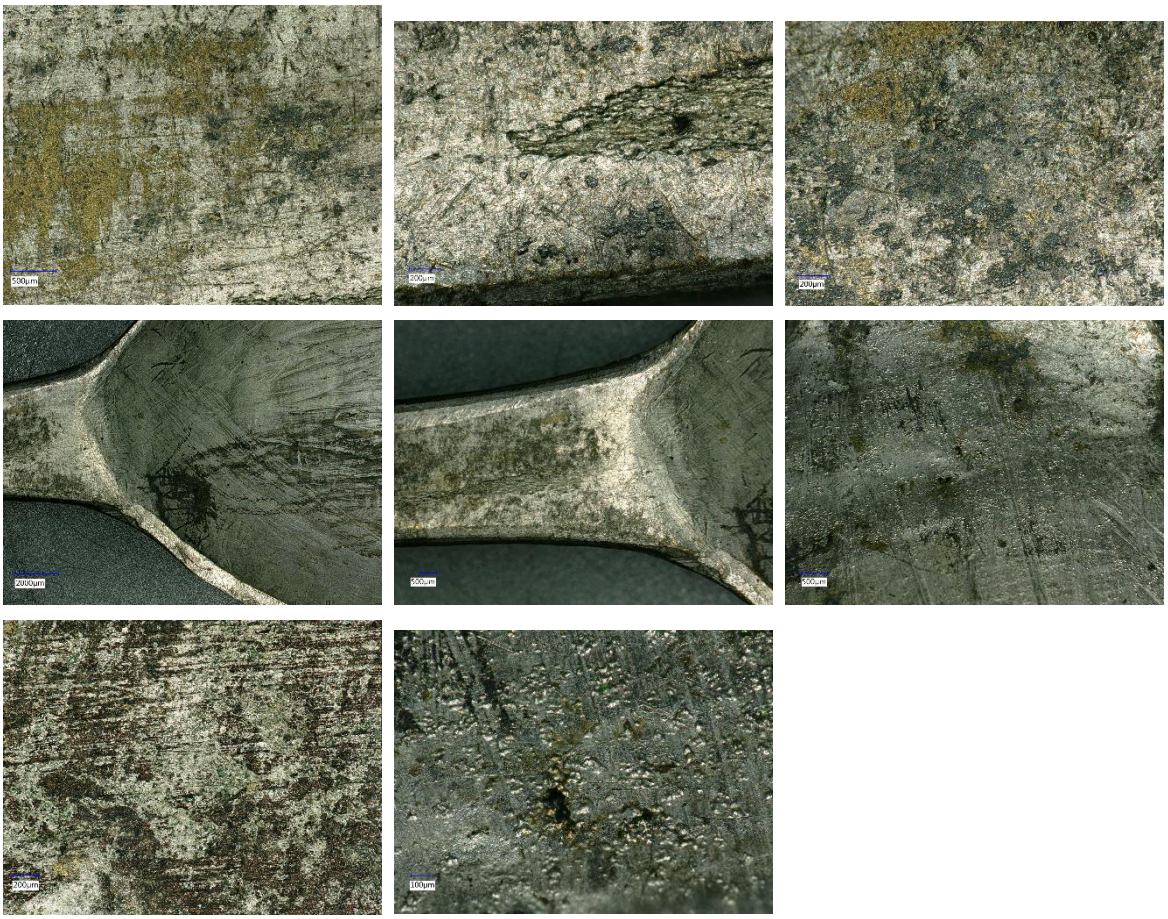
REM (Zeiss Supra 55 VP, Universität Wien)

Rückseite:





Lichtmikroskopaufnahmen (z-Scans; Keyence, VHX-5000), Universität für Bodenkultur Wien



Inventarnr.: 83939/54 **Alte Inventarnr.:** MdA4, 300

Sammlungsgr.: 530 Metallbearbeitung

akt. Standort: Standorte-TMW/TMW-Museum/E5/3-102

Titel: Galvanoplastisch erzeugter Löffel

Hersteller_in: Theyer, Franz; Waidele, Erwin

Ort: Wien

Datierung: 1840 **bis** 1845

Maße:

Breite 12.5 cm

Tiefe 2.1 cm

Höhe 0.5 cm

Beschreibung:

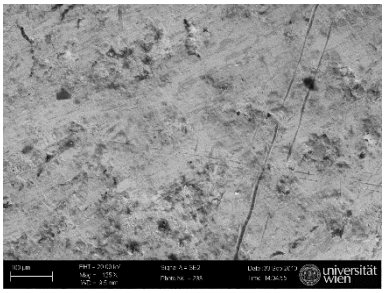
Befindet sich in Lade 2 (von oben gezählt) auf der mit schwarzem Stoff bespannten Tafel. Dort befinden sich lose die Objekte mit den Nummern 254, 258, 259, 260, 261, 262, 263, 266, 267, 269, 270, 271, 275, 289, 290, 293, 295, 296, 299, 300, 301, 303; montiert auf der Tafel sind die Objekte mit den Nummern 264, 265, 278-288, 291, 294, 297. Es fehlen die Objekte mit den Nummern 255, 256, 257, 268, 272, 273, 274, 276, 277, 292, 298, 302 und 304.

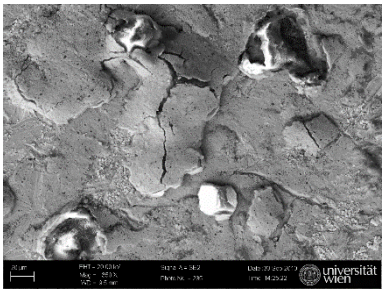
Schlagworte: Kupfer, versilbert

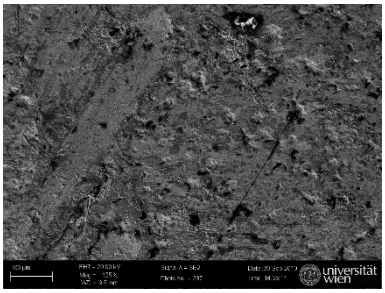
Digitalverweise:

REM, EDX (Zeiss Supra 55 VP, Universität Wien)

Rückseite:

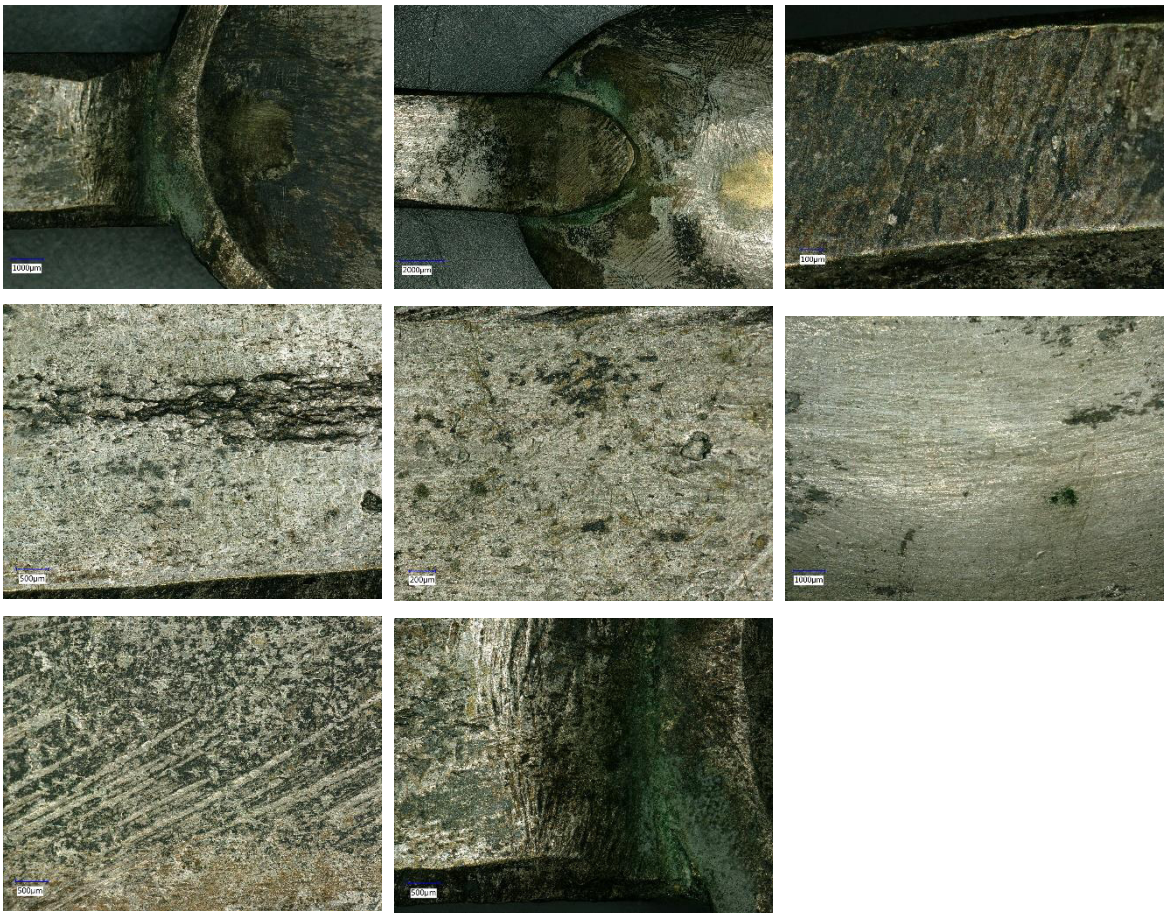






Element	Atomic%	Element	Atomic%	Element	Atomic%	Element	Atomic%
C	51,44	C	62,57	C	52,88	O	34,27
O	30,55	O	19,37	O	19,78	S	4,5
S	1,18	Si	0,35	S	0,58	Cu	31,37
Ca	0,21	S	0,56	Cu	10,31	Zn	15,58
Cu	4,74	Cu	10,17	Zn	4,01	Ag	14,28
Zn	1,62	Zn	2,99	Ag	12,43		
Ag	10,26	Ag	3,98				

Lichtmikroskopaufnahmen (z-Scans; Keyence, VHX-5000), Universität für Bodenkultur Wien



Inventarnr.: 83939/55 **Alte Inventarnr.:** MdA4, 301

Sammlungsgr.: 530 Metallbearbeitung

akt. Standort: Standorte-TMW/TMW-Museum/E5/3-102

Titel: Galvanoplastisch erzeugtes Medaillon

Hersteller_in: Theyer, Franz; Waidele, Erwin

Ort: Wien

Datierung: 1840 **bis** 1845

Maße:

Breite 5.7 cm

Tiefe 5 cm

Höhe 0.2 cm

Beschreibung:

Befindet sich in Lade 2 (von oben gezählt) auf der mit schwarzem Stoff bespannten Tafel. Dort befinden sich lose die Objekte mit den Nummern 254, 258, 259, 260, 261, 262, 263, 266, 267, 269, 270, 271, 275, 289, 290, 293, 295, 296, 299, 300, 301, 303; montiert auf der Tafel sind die Objekte mit den Nummern 264, 265, 278-288, 291, 294, 297. Es fehlen die Objekte mit den Nummern 255, 256, 257, 268, 272, 273, 274, 276, 277, 292, 298, 302 und 304.

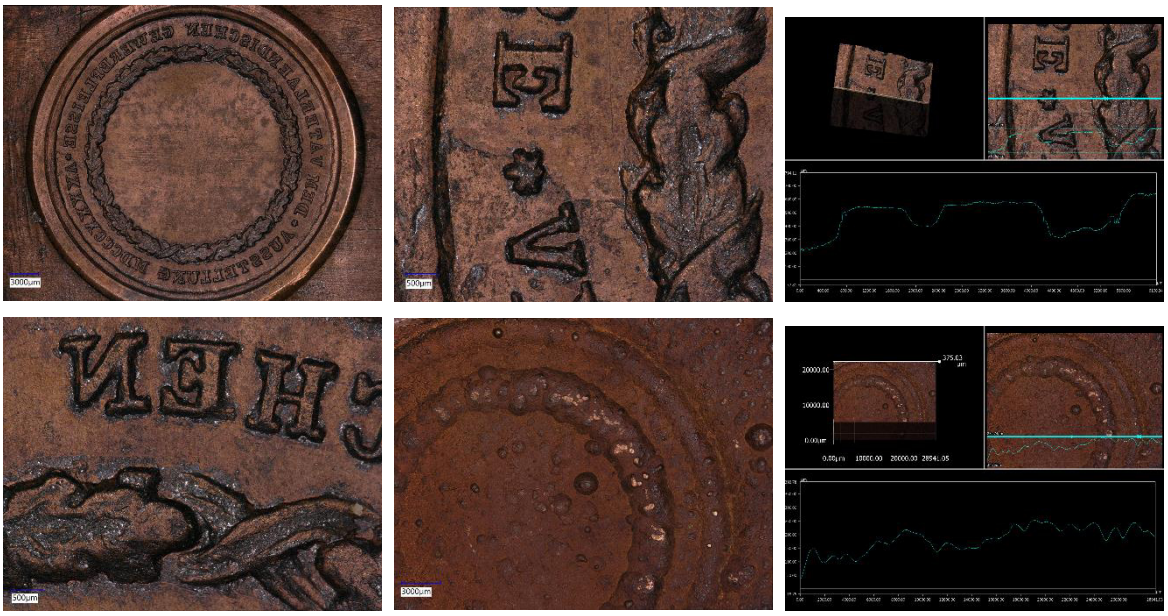
Schlagworte: Kupfer

Digitalverweise:

EDX (Zeiss Supra 55 VP, Universität Wien)

Element	Atomic%	Element	Atomic%	Element	Atomic%
C	69,44	C	70,55	C	55,58
O	19,09	O	20,13	O	30,34
Si	0,37	Si	0,26	Cu	9,08
Cu	11,1	Ca	0,39	Pb	5,01
		Cu	8,66		

Lichtmikroskopaufnahmen (z-Scans; Keyence, VHX-5000), Universität für Bodenkultur Wien



Inventarnr.: 83939/56 **Alte Inventarnr.:** MdA4, 303

Sammlungsgr.: 530 Metallbearbeitung

akt. Standort: Standorte-TMW/TMW-Museum/E5/3-102

Titel: Galvanoplastisch erzeugtes Medaillon

Hersteller_in: Theyer, Franz; Waidele, Erwin

Ort: Wien

Datierung: 1840 **bis** 1845

Maße:

Breite 9 cm

Tiefe 6 cm

Höhe 0.3 cm

Beschreibung:

Befindet sich in Lade 2 (von oben gezählt) auf der mit schwarzem Stoff bespannten Tafel. Dort befinden sich lose die Objekte mit den Nummern 254, 258, 259, 260, 261, 262, 263, 266, 267, 269, 270, 271, 275, 289, 290, 293, 295, 296, 299, 300, 301, 303; montiert auf der Tafel sind die Objekte mit den Nummern 264, 265, 278-288, 291, 294, 297. Es fehlen die Objekte mit den Nummern 255, 256, 257, 268, 272, 273, 274, 276, 277, 292, 298, 302 und 304.

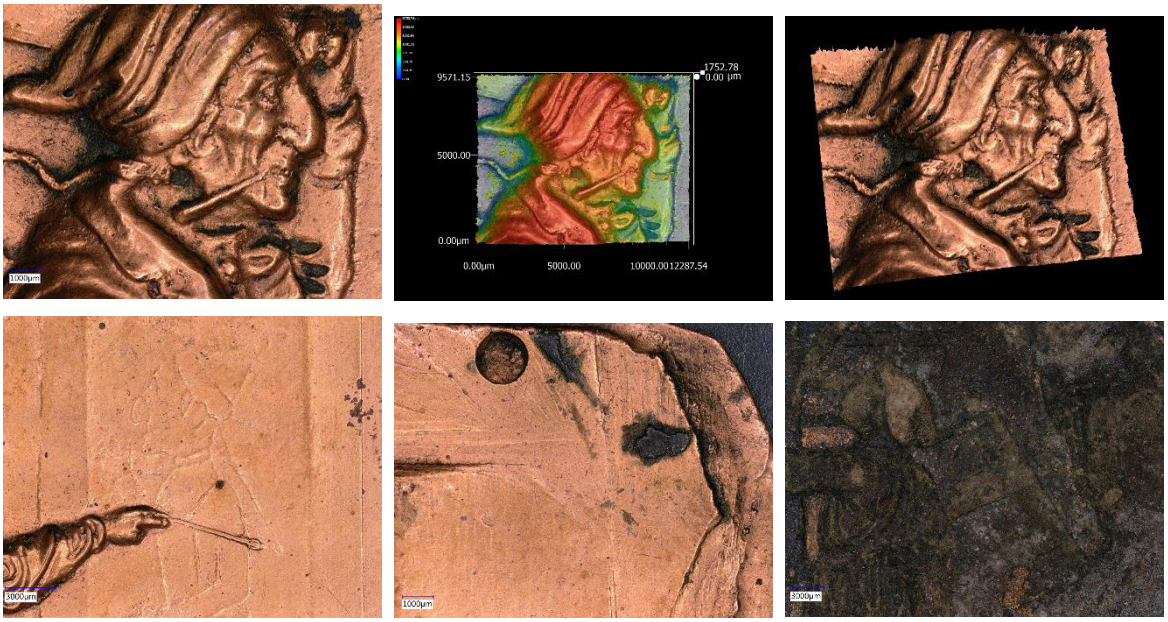
Schlagworte: Kupfer, versilbert

Digitalverweise:

EDX (Zeiss Supra 55 VP, Universität Wien)

Element	Atomic%	Element	Atomic%	Element	Atomic%
C	68,96	C	57,52	C	65,02
O	13	O	8,35	O	31,35
S	0,16	Cu	34,12	Mg	0,22
Cu	17,69			Si	0,33
Ag	0,19			S	0,4
				Ca	0,19
				Cu	2,4
				Ag	0,08

Lichtmikroskopaufnahmen (z-Scans; Keyence, VHX-5000), Universität für Bodenkultur Wien



Inventarnr.: 83939/58 **Alte Inventarnr.:** MdA4, 264

Sammlungsgr.: 530 Metallbearbeitung

akt. Standort: Standorte-TMW/TMW-Museum/E5/3-102

Titel: Galvanoplastisch erzeugtes Medaillon

Hersteller_in: Theyer, Franz; Waidele, Erwin

Ort: Wien

Datierung: 1840 **bis** 1845

Maße:

Breite 3.5 cm

Tiefe 4.5 cm

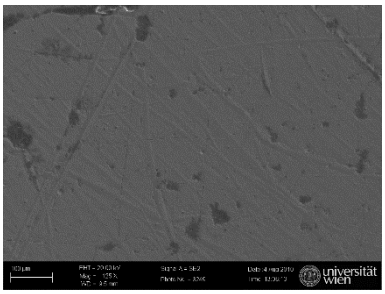
Höhe 0.5 cm

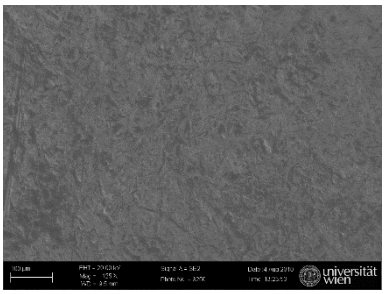
Beschreibung:

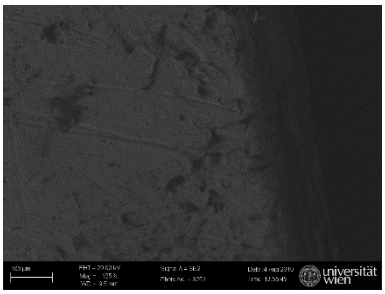
Schlagworte: Kupfer, vergoldet

Digitalverweise:

REM, EDX (Zeiss Supra 55 VP, Universität Wien)

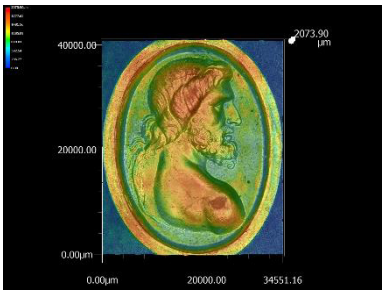


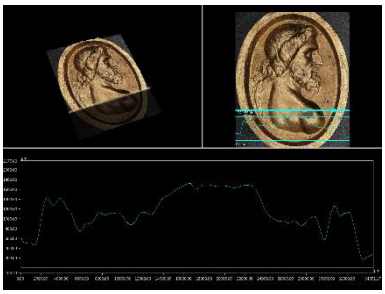


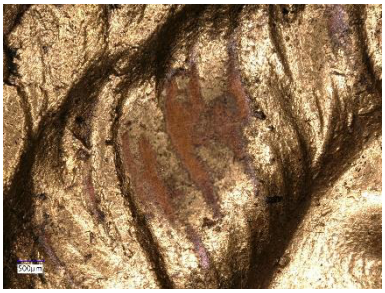


Element	Atomic%	Element	Atomic%	Element	Atomic%
C	55,03	C	63,67	C	77,24
O	9,18	O	27,08	O	11,07
Cu	17,67	Si	0,57	Cu	4,54
Au	14,96	Ca	0,18	Ag	0,13
Hg	3,16	Cu	6,23	Au	7,02
		Au	1,95		

Lichtmikroskopaufnahmen (z-Scans; Keyence, VHX-5000), Universität für Bodenkultur Wien







Inventarnr.: 83939/59 **Alte Inventarnr.:** MdA4, 265

Sammlungsgr.: 530 Metallbearbeitung

akt. Standort: Standorte-TMW/TMW-Museum/E5/3-102

Titel: Galvanoplastisch erzeugtes Medaillon

Hersteller_in: Theyer, Franz; Waidele, Erwin

Ort: Wien

Datierung: 1840 **bis** 1845

Maße:

Breite 3.8 cm

Tiefe 4.8 cm

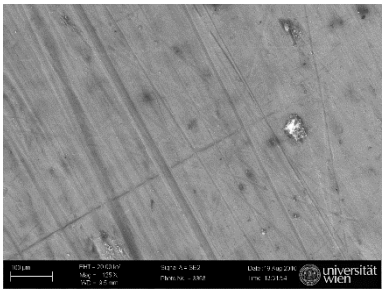
Höhe 0.5 cm

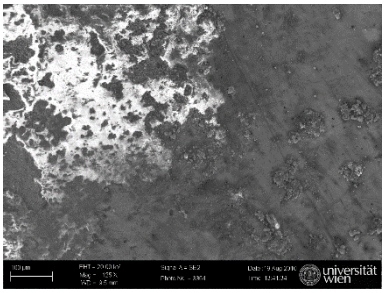
Beschreibung:

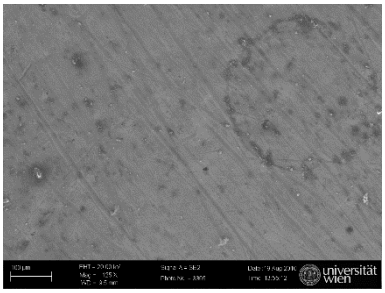
Schlagworte: Kupfer, versilbert

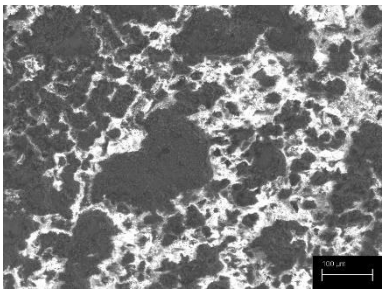
Digitalverweise:

REM, EDX (Zeiss Supra 55 VP, Universität Wien)

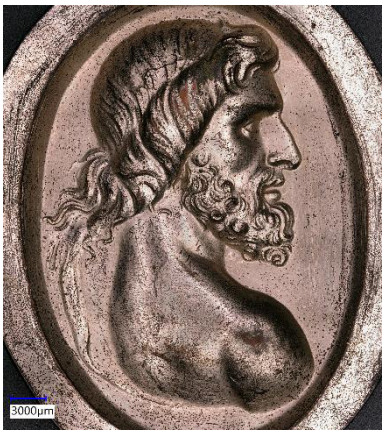


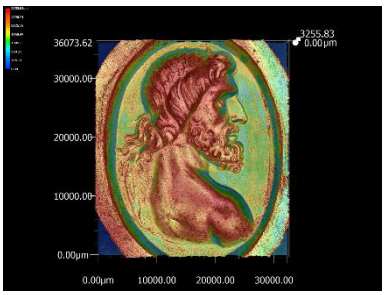




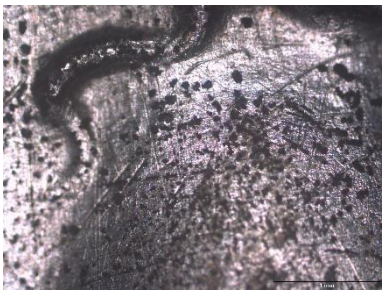


Lichtmikroskopaufnahmen (z-Scans; Keyence, VHX-5000), Universität für Bodenkultur Wien





Lichtmikroskopaufnahmen (Olympus GX51, Happy Platting GmbH, Wiener Neustadt)



Inventarnr.: 83939/60 **Alte Inventarnr.:** MdA4, 278

Sammlungsgr.: 530 Metallbearbeitung

akt. Standort: Standorte-TMW/TMW-Museum/E5/3-102

Titel: Galvanoplastisch erzeugtes Medaillon

Hersteller_in: Theyer, Franz; Waidele, Erwin

Ort: Wien

Datierung: 1840 **bis** 1845

Maße:

Breite 2.8 cm

Tiefe 3.2 cm

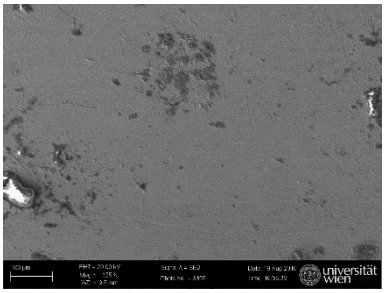
Höhe 0.5 cm

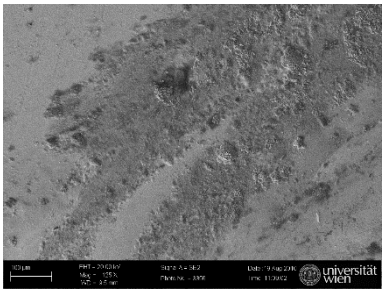
Beschreibung:

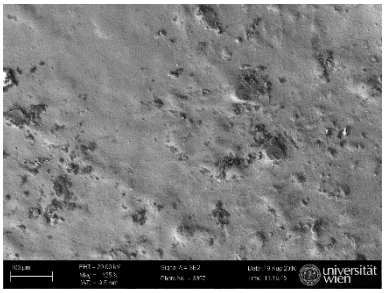
Schlagworte: Kupfer, versilbert, vergoldet

Digitalverweise:

REM, EDX (Zeiss Supra 55 VP, Universität Wien)

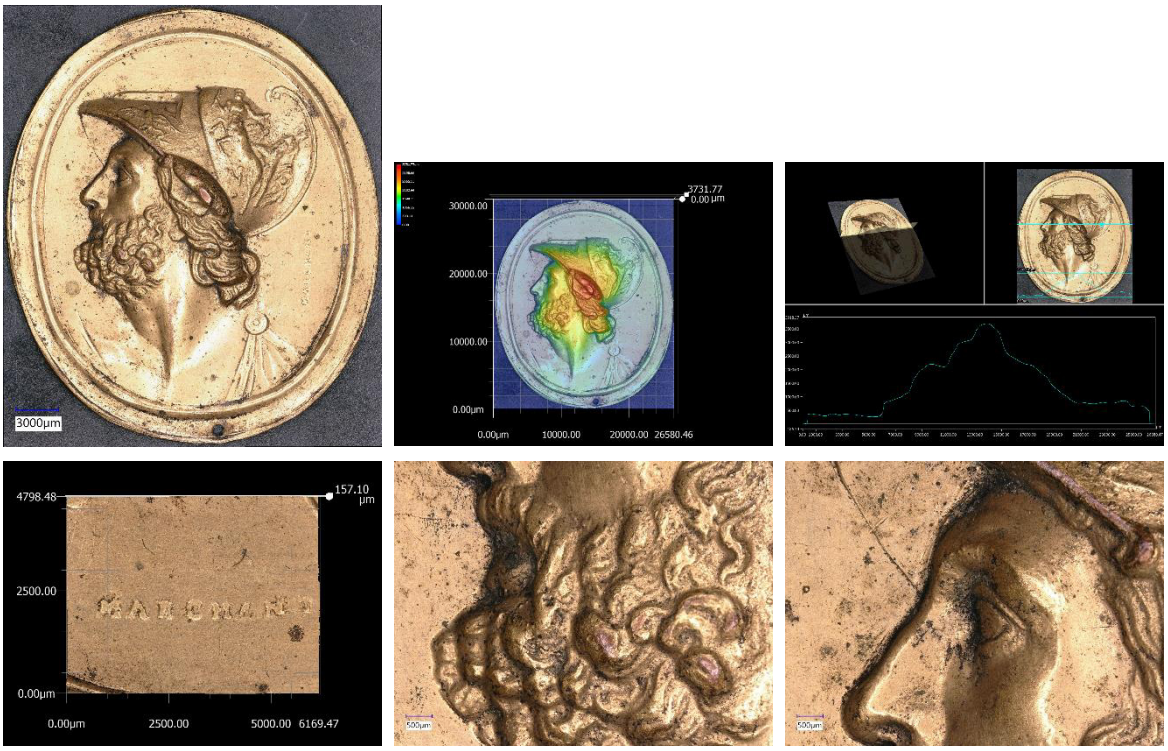






Element	Atomic%	Element	Atomic%	Element	Atomic%	Element	Atomic%
C	67,8	C	48,94	C	55,43	C	57,42
O	20,32	O	32,28	O	21,63	O	19,37
Cu	3,61	Mg	0,46	S	2,8	Ca	0,35
Au	8,28	Al	0,51	Ca	0,36	Cu	16,34
		Si	1,22	Cu	15,66	Ag	1,53
		S	0,48	Ag	1,12	Au	4,99
		Cl	0,53	Au	2,99		
		Ca	0,91				
		Cu	8,96				
		Ag	1,26				
		Au	4,99				
		C	48,94				

Lichtmikroskopaufnahmen (z-Scans; Keyence, VHX-5000), Universität für Bodenkultur Wien



Inventarnr.: 83939/61 **Alte Inventarnr.:** MdA4, 279

Sammlungsgr.: 530 Metallbearbeitung

akt. Standort: Standorte-TMW/TMW-Museum/E5/3-102

Titel: Galvanoplastisch erzeugtes Medaillon

Hersteller_in: Theyer, Franz; Waidele, Erwin

Ort: Wien

Datierung: 1840 **bis** 1845

Maße:

Breite 2.3 cm

Tiefe 3 cm

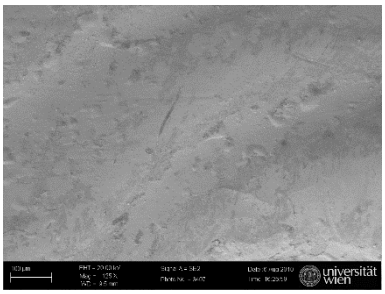
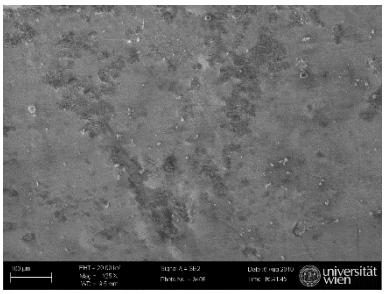
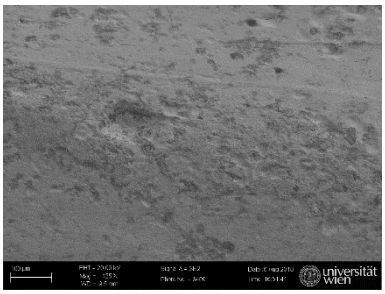
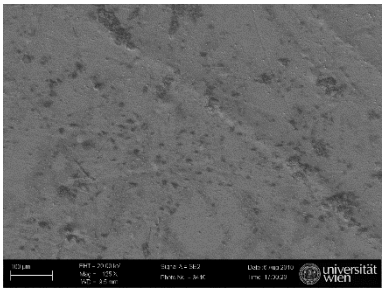
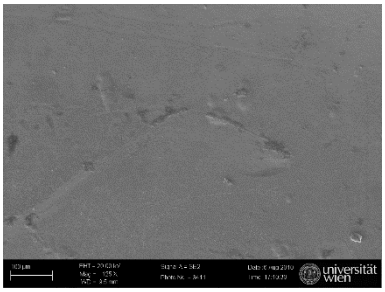
Höhe 0.5 cm

Beschreibung:

Schlagworte: Kupfer, versilbert, vergoldet

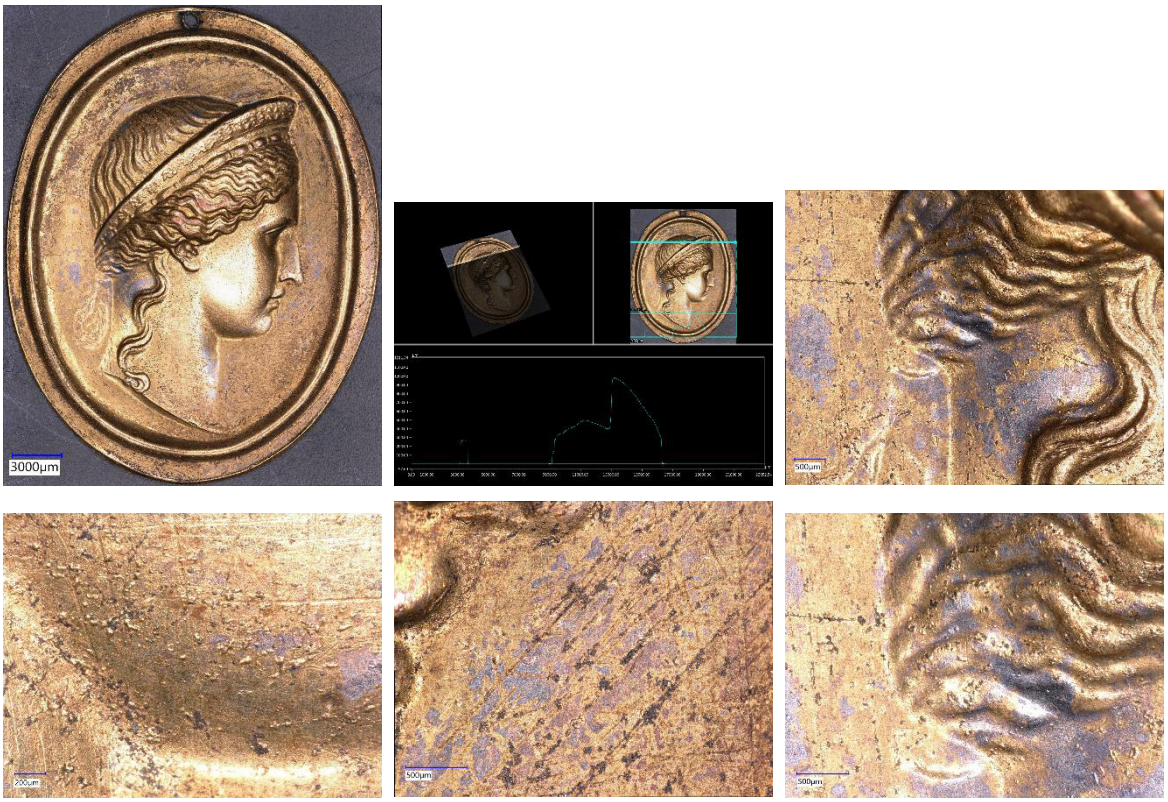
Digitalverweise:

REM, EDX (Zeiss Supra 55 VP, Universität Wien)

Element	Atomic%	Atomic%	Atomic%	Atomic%	Atomic%	Atomic%
C	41,11	51,66	64,55	54,33	51,41	31,61
O	37,76	19,56	16,7	24,58	33,46	9,41
Si			0,41			
S			6,06	5,02	4,25	
Cl				0,29		0,32
Ca	0,39		0,23	0,26		
Cu	5,26	15,95	5	4,12	0,32	8,07
Ag	4,61	1	4,88	3,75	2,19	20,2
Pt						3,15
Au	10,85	11,06	2,16	7,64	8,38	27,23
Pb		0,77				

Lichtmikroskopaufnahmen (z-Scans; Keyence, VHX-5000), Universität für Bodenkultur Wien



Inventarnr.: 83939/62 **Alte Inventarnr.:** MdA4, 280

Sammlungsgr.: 530 Metallbearbeitung

akt. Standort: Standorte-TMW/TMW-Museum/E5/3-102

Titel: Galvanoplastisch erzeugtes Medaillon

Hersteller_in: Theyer, Franz; Waidele, Erwin

Ort: Wien

Datierung: 1840 **bis** 1845

Maße:

Breite 3.4 cm

Tiefe 2.8 cm

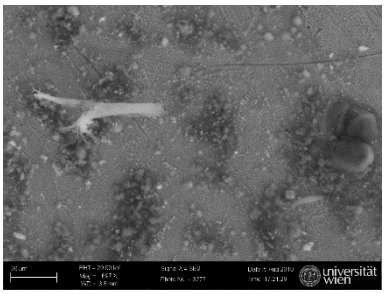
Höhe 0.5 cm

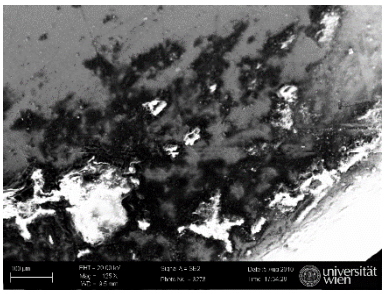
Beschreibung:

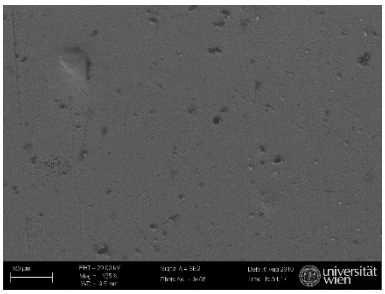
Schlagworte: Kupfer, versilbert, vergoldet

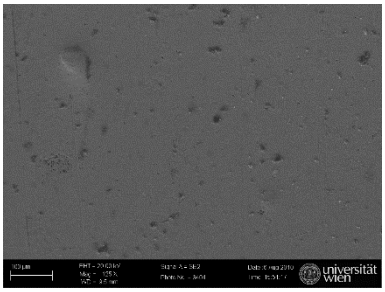
Digitalverweise:

REM, EDX (Zeiss Supra 55 VP, Universität Wien)









Element	Atomic%	Element	Atomic%	Element	Atomic%	Element	Atomic%
C	70,83	C	65,39	C	53,82	C	69,64
O	12,33	O	15,92	O	13,11	O	16,54
Mg	0,26	Mg	0,26	Cu	25,86	Si	0,5
Si	0,28	Al	0,21	Ag	0,29	Ca	0,49
S	3,14	Si	0,41	Au	6,92	Fe	0,16
Ca	0,36	Cl	0,15			Cu	10,31
Cu	11,66	K	0,19			Ag	0,21
Ag	0,13	Ca	0,26			Au	2,17
Au	1,01	Fe	0,13				
		Cu	3,21				
		Ag	0,11				
		Au	1,86				

Lichtmikroskopaufnahmen (z-Scans; Keyence, VHX-5000), Universität für Bodenkultur Wien

Inventarnr.: 83939/63 **Alte Inventarnr.:** MdA4, 281

Sammlungsgr.: 530 Metallbearbeitung

akt. Standort: Standorte-TMW/TMW-Museum/E5/3-102

Titel: Galvanoplastisch erzeugtes Medaillon

Hersteller_in: Theyer, Franz; Waidele, Erwin

Ort: Wien

Datierung: 1840 **bis** 1845

Maße:

Breite 2.6 cm

Tiefe 2.8 cm

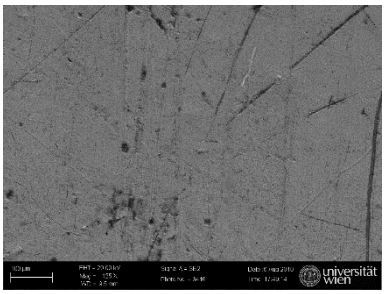
Höhe 0.5 cm

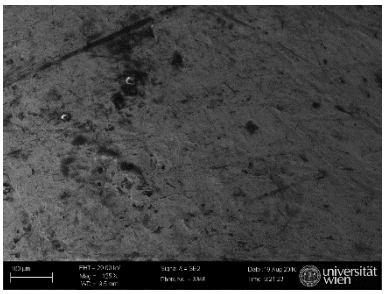
Beschreibung:

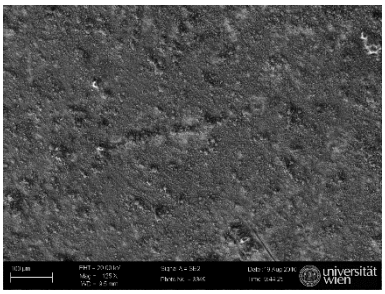
Schlagworte: Kupfer, vergoldet

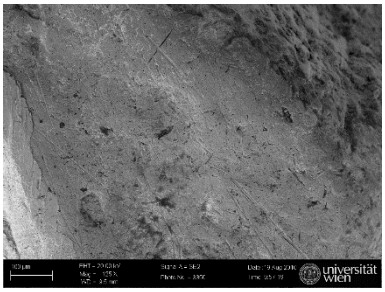
Digitalverweise:

REM, EDX (Zeiss Supra 55 VP, Universität Wien)



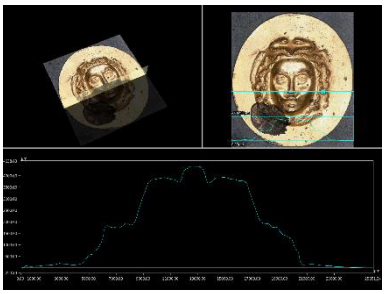


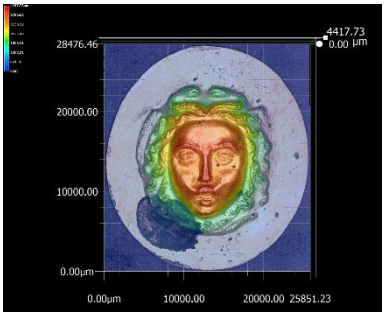


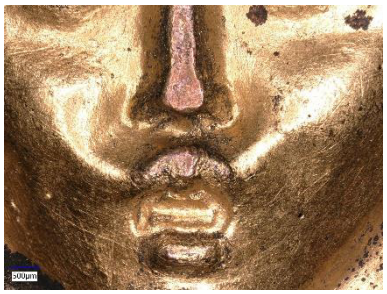


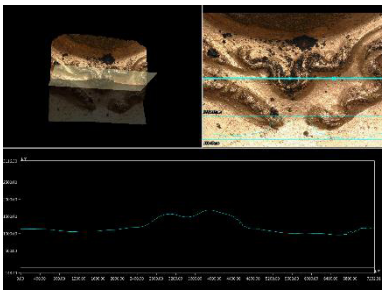
Element	Atomic%	Element	Atomic%
C	67,66	C	58,45
O	20,65	O	27,75
Si	0,68	Si	0,25
Cl	0,3	S	2,8
K	0,6	Cl	1,16
Ca	0,46	Ca	0,2
Cu	6,8	Cu	8,62
Au	2,85	Au	0,77

Lichtmikroskopaufnahmen (z-Scans; Keyence, VHX-5000), Universität für Bodenkultur Wien

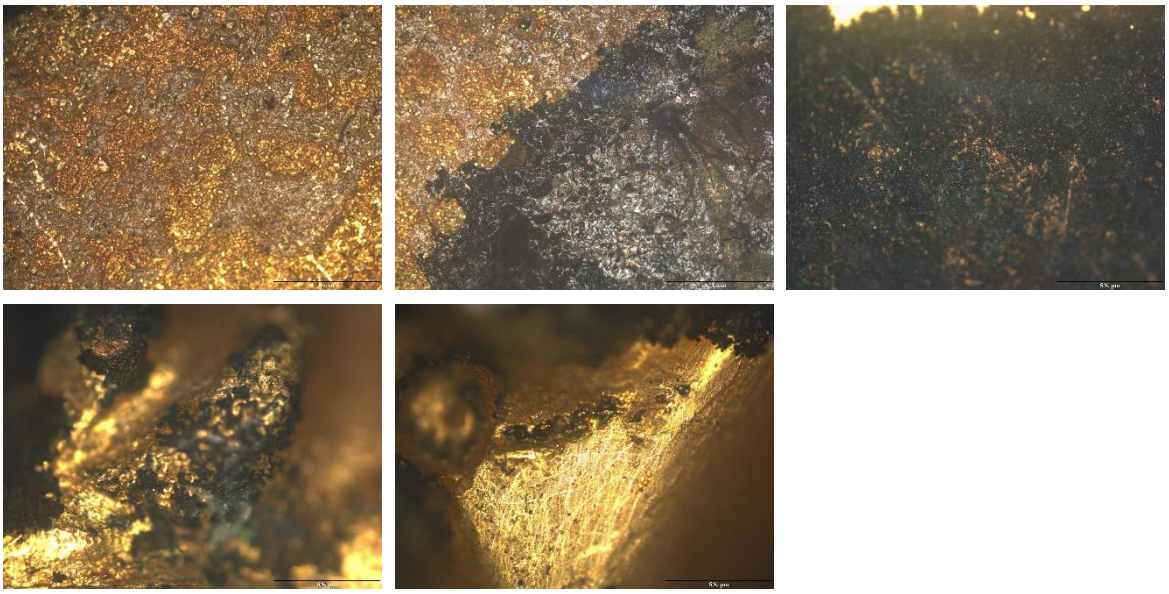








Lichtmikroskopaufnahmen (Olympus GX51, Happy Platting GmbH, Wiener Neustadt)



Inventarnr.: 83939/64 **Alte Inventarnr.:** MdA4, 282

Sammlungsgr.: 530 Metallbearbeitung

akt. Standort: Standorte-TMW/TMW-Museum/E5/3-102

Titel: Galvanoplastisch erzeugtes Medaillon

Hersteller_in: Theyer, Franz; Waidele, Erwin

Ort: Wien

Datierung: 1840 **bis** 1845

Maße:

Breite 2.6 cm

Tiefe 3.2 cm

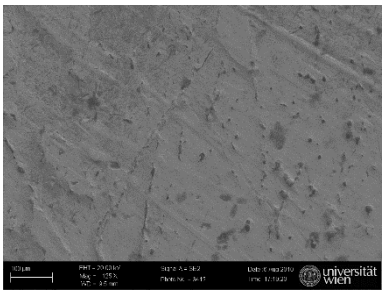
Höhe 0.5 cm

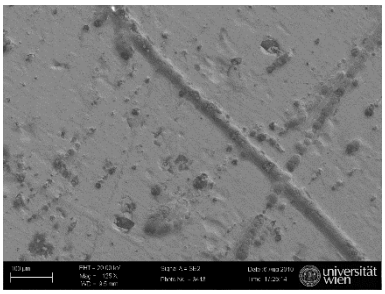
Beschreibung:

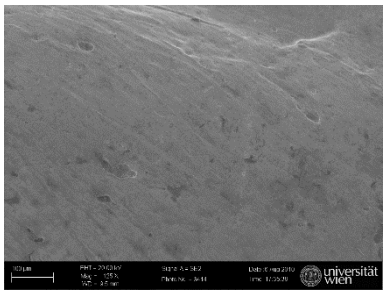
Schlagworte: Kupfer, versilbert, vergoldet

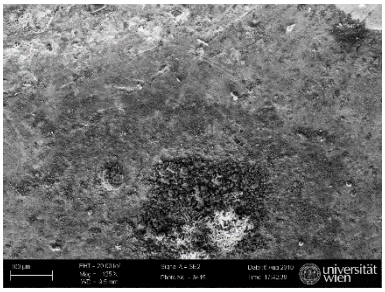
Digitalverweise:

REM, EDX (Zeiss Supra 55 VP, Universität Wien)



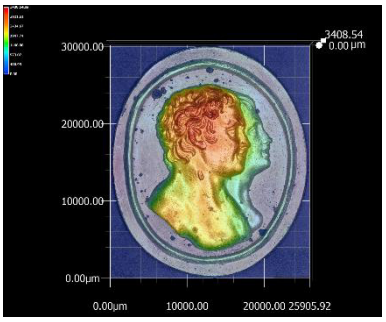


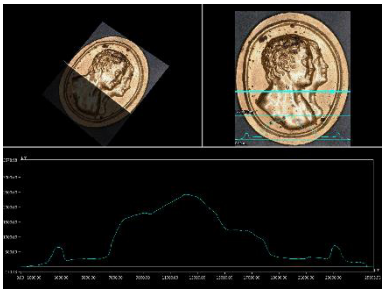




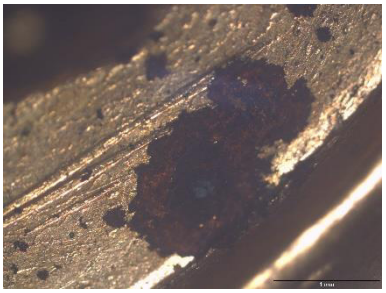
Element	Atomic%	Element	Atomic%	Element	Atomic%	Element	Atomic%
C	59,77	C	57,33	C	63,69	C	48,09
O	15,94	O	15,68	O	12,74	O	18,39
Cu	16,78	Ca	0,1	Cu	13,35	Mg	1,43
Au	7,51	Cu	20,84	Au	9,67	S	3
		Ag	0,14	Hg	0,55	Ca	0,14
		Au	5,91			Cu	6,18
						Au	1,68

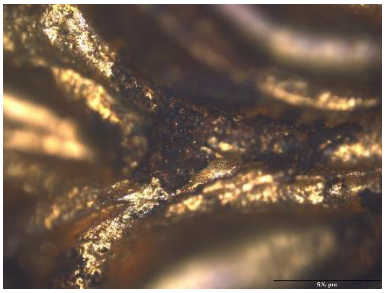
Lichtmikroskopaufnahmen (Olympus GX51, Happy Platting GmbH, Wiener Neustadt)





Lichtmikroskopaufnahmen Happy Platting, Wiener Neustadt





Inventarnr.: 83939/65 **Alte Inventarnr.:** MdA4, 283

Sammlungsgr.: 530 Metallbearbeitung

akt. Standort: Standorte-TMW/TMW-Museum/E5/3-102

Titel: Galvanoplastisch erzeugtes Medaillon

Hersteller_in: Theyer, Franz; Waidele, Erwin

Ort: Wien

Datierung: 1840 **bis** 1845

Maße:

Breite 2.7 cm

Tiefe 3.2 cm

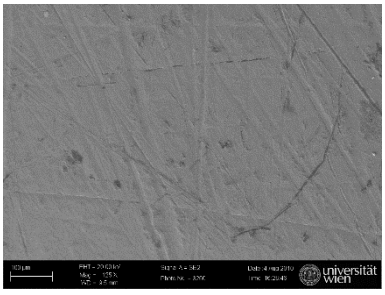
Höhe 0.5 cm

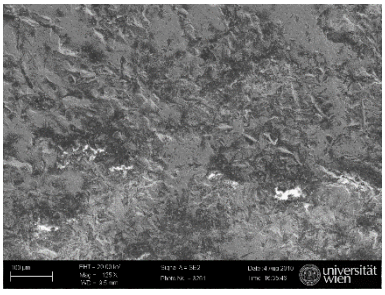
Beschreibung:

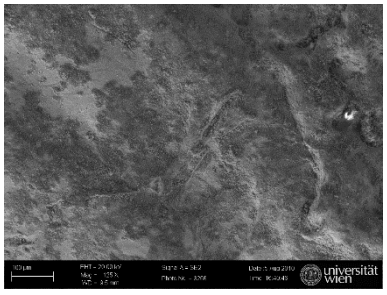
Schlagworte: Kupfer, versilbert, vergoldet

Digitalverweise:

REM, EDX (Zeiss Supra 55 VP, Universität Wien)

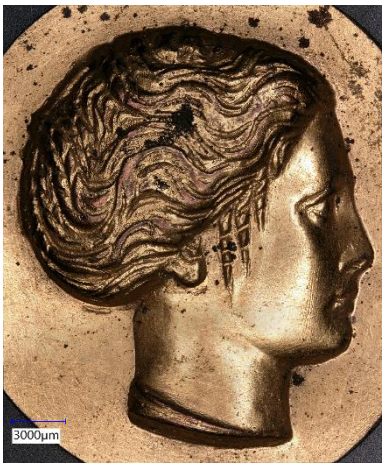


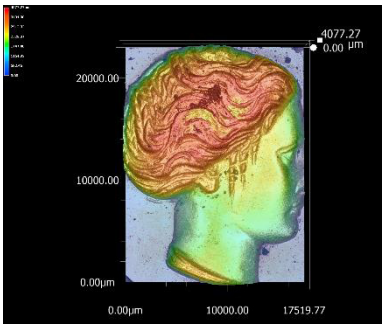


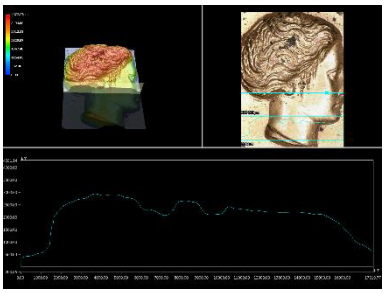


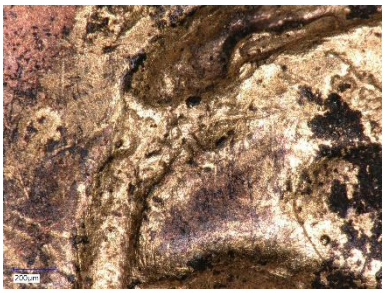
Element	Atomic%	Element	Atomic%	Element	Atomic%	Element	Atomic%
C	58,78	C	62,58	C	60,46	C	66,95
O	16,18	O	31,1	O	21,7	O	14,22
Cu	21,56	S	0,57	Si	0,4	Si	0,15
Au	3,13	Cl	0,23	S	4,55	S	2,57
Hg	0,36	Ca	0,66	Ca	0,28	Cl	0,63
		Cu	4,17	Cu	11,99	Ca	0,13
		Ag	0,26	Au	0,62	Cu	9,34
		Au	0,43			Au	0,42

Lichtmikroskopaufnahmen (z-Scans; Keyence, VHX-5000), Universität für Bodenkultur Wien

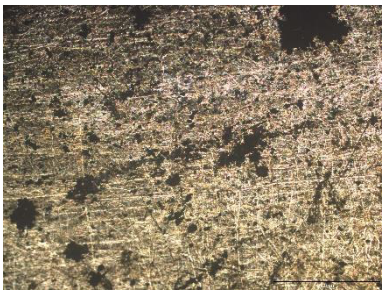


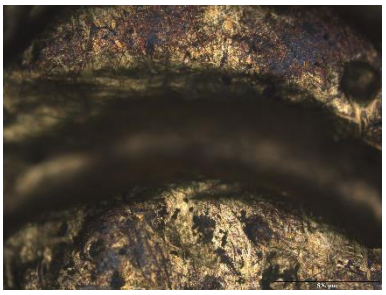


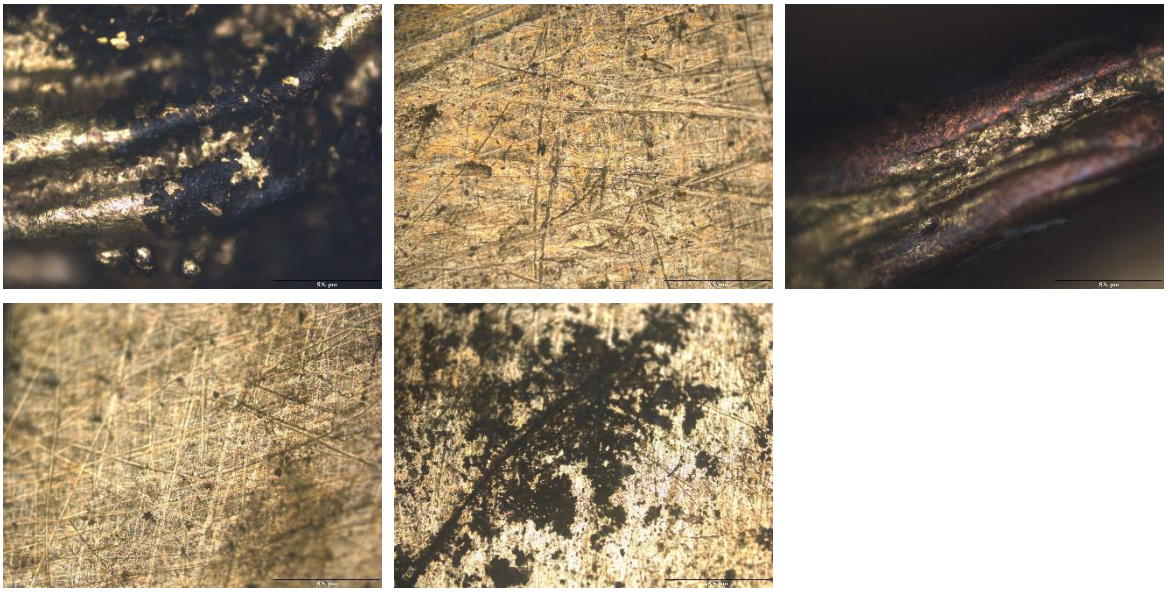




Lichtmikroskopaufnahmen (Olympus GX51, Happy Platting GmbH, Wiener Neustadt)



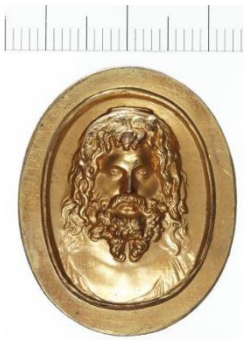




Inventarnr.: 83939/66 **Alte Inventarnr.:** MdA4, 284

Sammlungsgr.: 530 Metallbearbeitung

akt. Standort: Standorte-TMW/TMW-Museum/E5/3-102



Titel: Galvanoplastisch erzeugtes Medaillon

Hersteller_in: Theyer, Franz; Waidele, Erwin

Ort: Wien

Datierung: 1840 **bis** 1845

Maße:

Breite 2.9 cm

Tiefe 3.5 cm

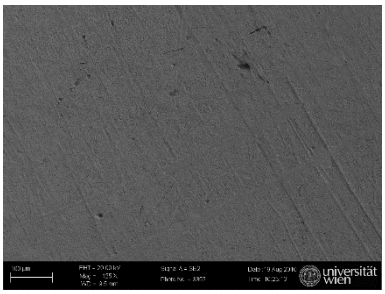
Höhe 0.5 cm

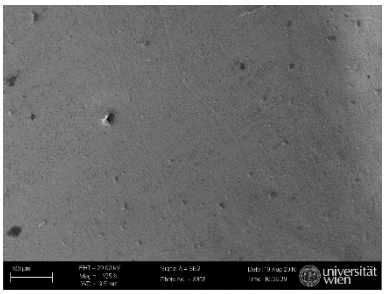
Beschreibung:

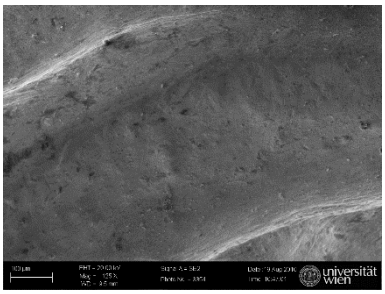
Schlagworte: Kupfer, versilbert, vergoldet

Digitalverweise:

REM, EDX (Zeiss Supra 55 VP, Universität Wien)

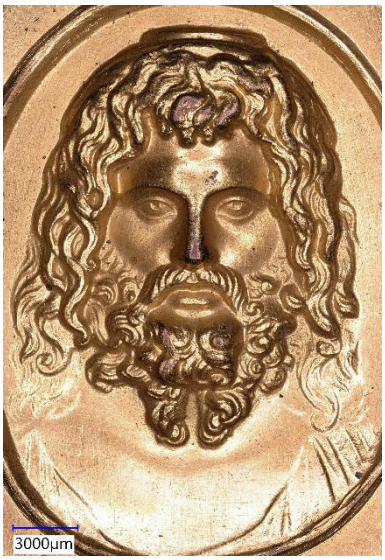


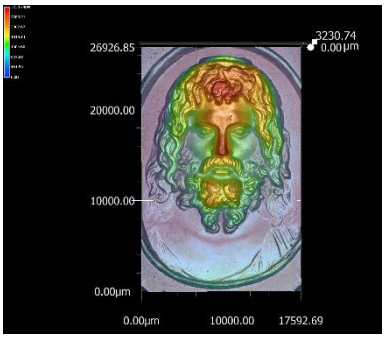


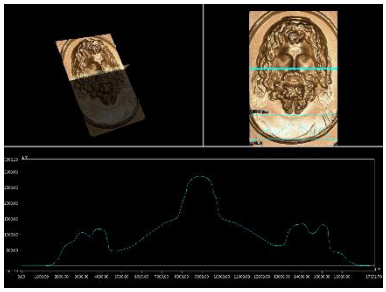


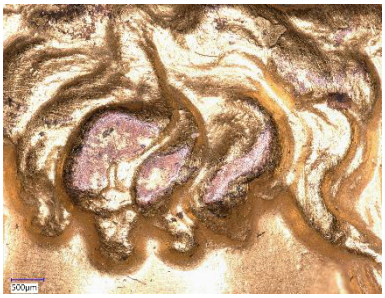
Element	Atomic%	Element	Atomic%	Element	Atomic%
C	55,04	C	50,33	C	64,13
O	18,81	O	13,5	O	13,8
Si	0,68	Cu	7,03	Cu	3,63
S	0,77	Ge	5,7	Ge	3,39
Cu	24,69	Ag	0,45	Nb	7,35
		Au	23	Au	7,7

Lichtmikroskopaufnahmen (z-Scans; Keyence, VHX-5000), Universität für Bodenkultur Wien









Inventarnr.: 83939/67 **Alte Inventarnr.:** MdA4, 285

Sammlungsgr.: 530 Metallbearbeitung

akt. Standort: Standorte-TMW/TMW-Museum/E5/3-102

Objektbez.:

Titel: Galvanoplastisch erzeugtes Medaillon

Hersteller_in: Theyer, Franz; Waidele, Erwin

Ort: Wien

Datierung: 1840 **bis** 1845

Maße:

Breite 3 cm

Tiefe 3.2 cm

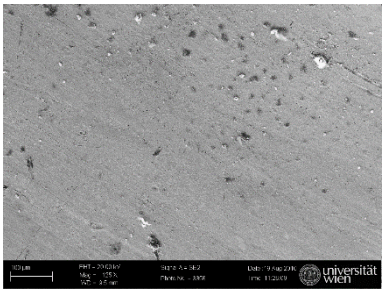
Höhe 0.5 cm

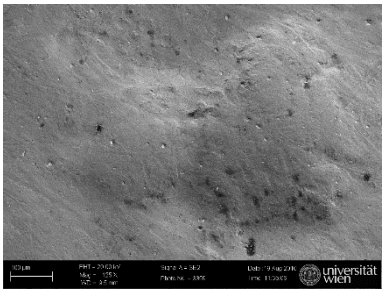
Beschreibung:

Schlagworte: Kupfer, versilbert, vergoldet

Digitalverweise:

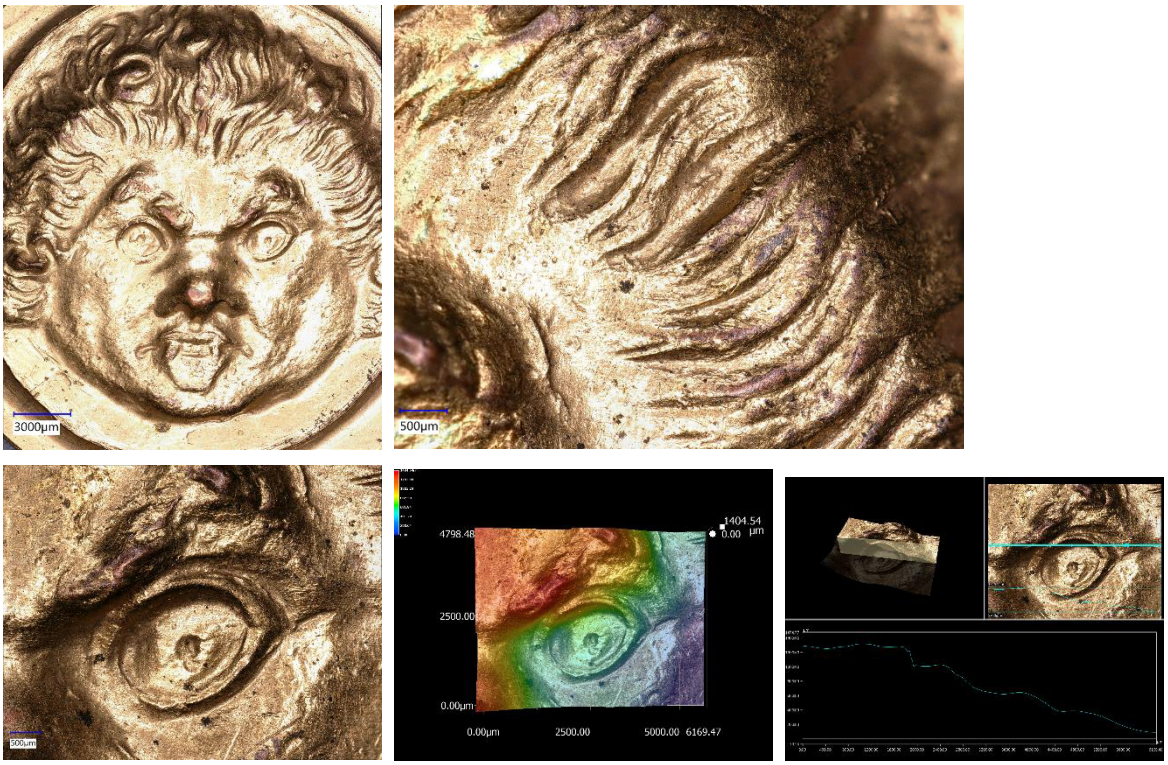
REM, EDX (Zeiss Supra 55 VP, Universität Wien)





Element	Atomic%	Element	Atomic%
C	55,37	C	58,51
O	15,7	O	16
Cu	21,96	Cu	20,94
Ag	0,25	Au	4,55
Au	6,73		

Lichtmikroskopaufnahmen (z-Scans; Keyence, VHX-5000), Universität für Bodenkultur Wien



Inventarnr.: 83939/68 **Alte Inventarnr.:** MdA4, 286

Sammlungsgr.: 530 Metallbearbeitung

akt. Standort: Standorte-TMW/TMW-Museum/E5/3-102

Titel: Galvanoplastisch erzeugtes Medaillon

Hersteller_in: Theyer, Franz; Waidele, Erwin

Ort: Wien

Datierung: 1840 **bis** 1845

Maße:

Breite 3.5 cm

Tiefe 2.9 cm

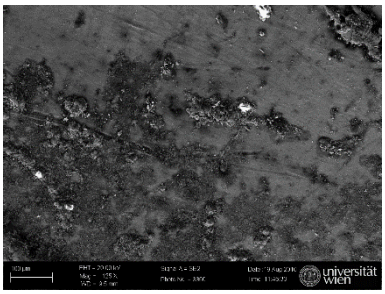
Höhe 0.5 cm

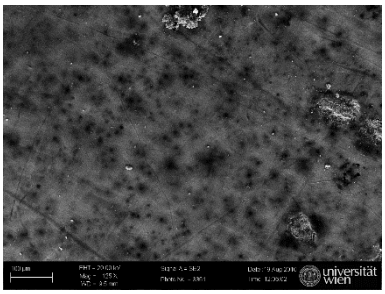
Beschreibung:

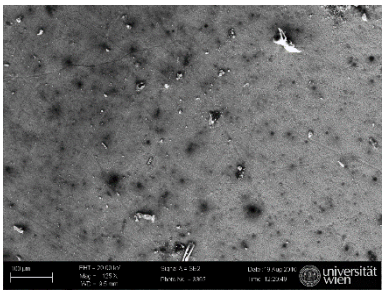
Schlagworte: Kupfer, versilbert

Digitalverweise:

REM, EDX (Zeiss Supra 55 VP, Universität Wien)







Element	Atomic%	Element	Atomic%	Element	Atomic%
C	60,82	C	72,77	C	71,73
O	24,25	O	21,05	O	19,1
Si	0,22	S	0,19	Cu	7,44
S	2,17	Cu	4,42	Ag	1,73
Cu	10,2	Ag	1,57		
Ag	2,35				

Lichtmikroskopaufnahmen (z-Scans; Keyence, VHX-5000), Universität für Bodenkultur Wien

Inventarnr.: 83939/69 **Alte Inventarnr.:** MdA4, 287

Sammlungsgr.: 530 Metallbearbeitung

akt. Standort: Standorte-TMW/TMW-Museum/E5/3-102

Titel: Galvanoplastisch erzeugtes Medaillon

Hersteller_in: Theyer, Franz; Waidele, Erwin

Ort: Wien

Datierung: 1840 **bis** 1845

Maße:

Breite 2.6 cm

Tiefe 3.3 cm

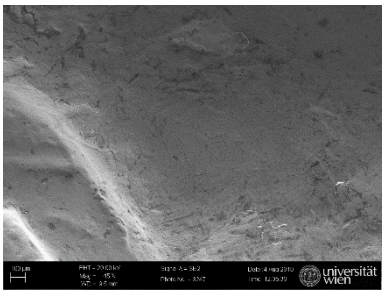
Höhe 0.5 cm

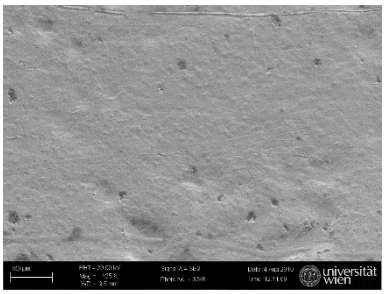
Beschreibung:

Schlagworte: Kupfer, vergoldet

Digitalverweise:

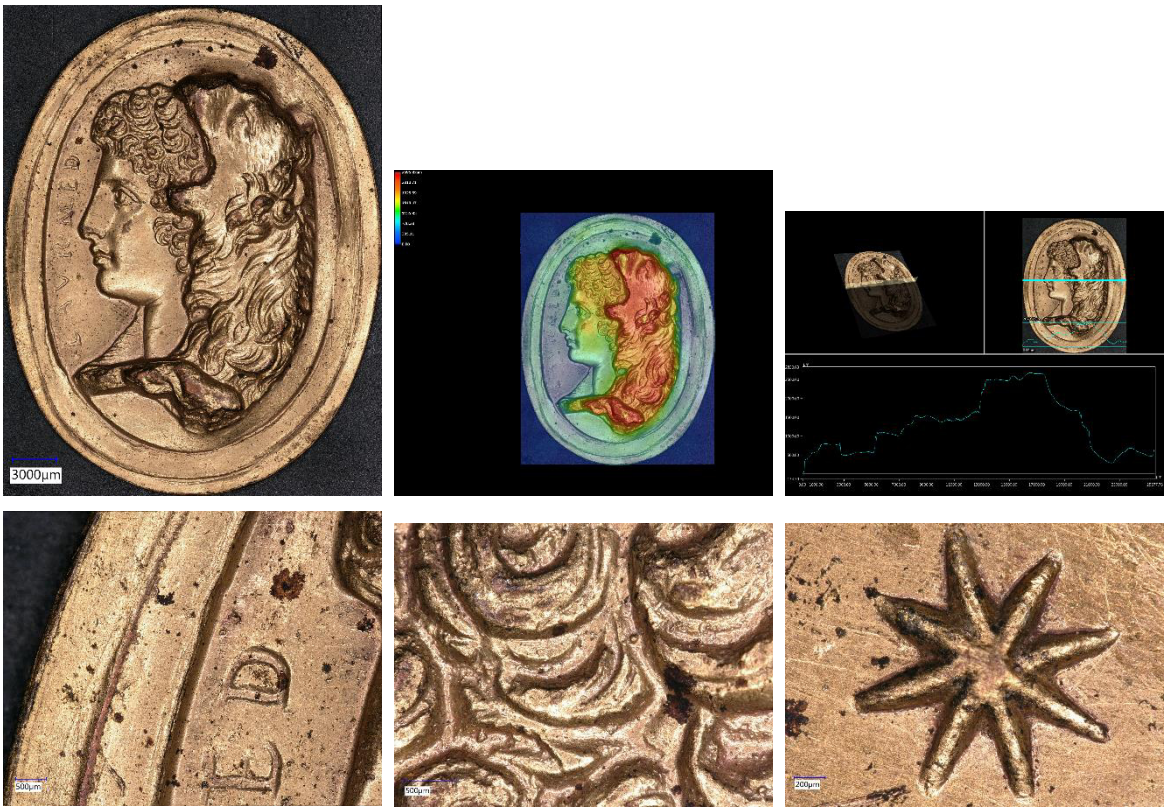
REM, EDX (Zeiss Supra 55 VP, Universität Wien)





Element	Atomic%	Element	Atomic%	Element	Atomic%
C	58,66	C	35,24	C	59,98
O	18,57	O	11,61	O	12,66
Mg	0,58	S	0,75	Cu	23,26
Al	0,23	Fe	0,22	Au	4,11
Si	0,54	Cu	21,39		
S	2,78	Au	0,52		
Cu	11,61				
Au	0,51				

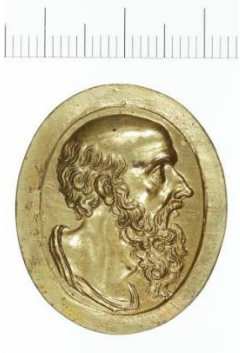
Lichtmikroskopaufnahmen (z-Scans; Keyence, VHX-5000), Universität für Bodenkultur Wien



Inventarnr.: 83939/70 **Alte Inventarnr.:** MdA4, 288

Sammlungsgr.: 530 Metallbearbeitung

akt. Standort: Standorte-TMW/TMW-Museum/E5/3-102



Titel: Galvanoplastisch erzeugtes Medaillon

Hersteller_in: Theyer, Franz; Waidele, Erwin

Ort: Wien

Datierung: 1840 **bis** 1845

Maße:

Breite 2.8 cm

Tiefe 3.3 cm

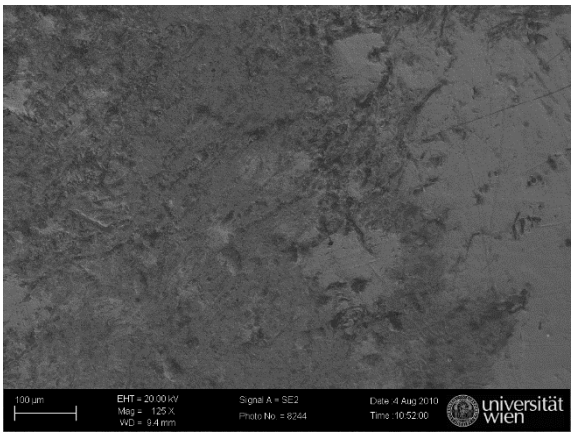
Höhe 0.5 cm

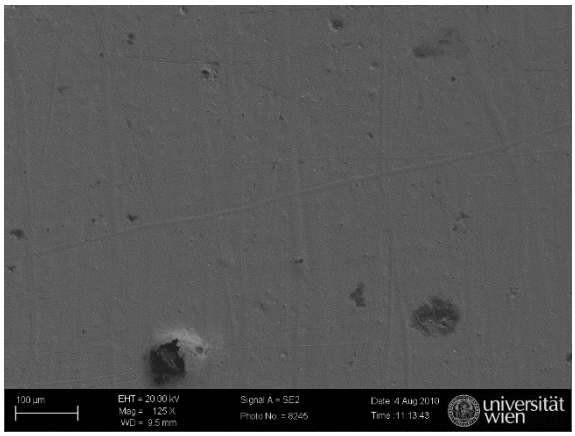
Beschreibung:

Schlagworte: Kupfer, versilbert, vergoldet

Digitalverweise:

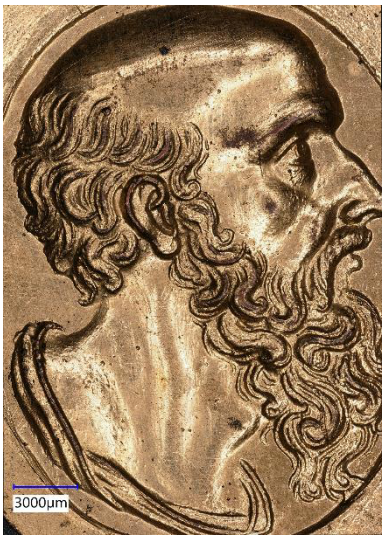
REM, EDX (Zeiss Supra 55 VP, Universität Wien)

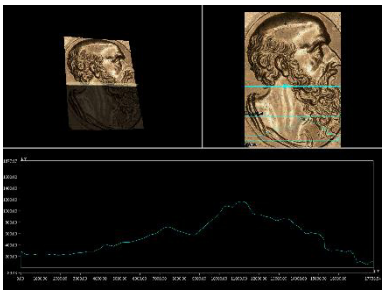


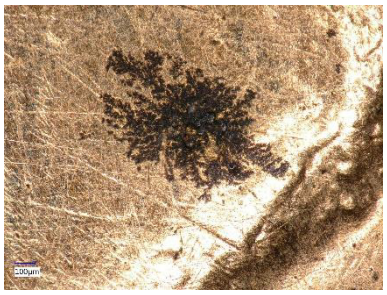


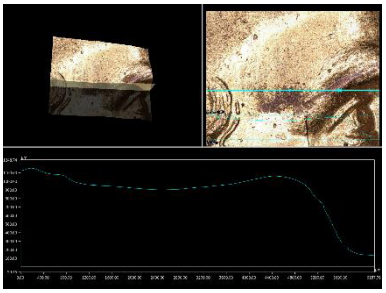
Element	Atomic%	Element	Atomic%	Element	Atomic%
C	63,59	C	54,17	C	38,7
O	24,99	O	11,97	O	10,18
Si	0,43	Cu	21,54	S	0,29
Ca	0,14	Ag	0,5	Cu	0,5
Cu	7,22	Au	11,02	Ag	1,52
Ge	0,45	Hg	0,8	Au	0,07
Nb	1,51			Hg	1,82
Ag	0,09				
Au	1,41				

Lichtmikroskopaufnahmen (z-Scans; Keyence, VHX-5000), Universität für Bodenkultur Wien









Inventarnr.: 83939/71 **Alte Inventarnr.:** MdA4, 291

Sammlungsgr.: 530 Metallbearbeitung

akt. Standort: Standorte-TMW/TMW-Museum/E5/3-102

Titel: Galvanoplastisch erzeugtes Medaillon

Hersteller_in: Theyer, Franz; Waidele, Erwin

Ort: Wien

Datierung: 1840 **bis** 1845

Maße:

Breite 3.7 cm

Tiefe 3 cm

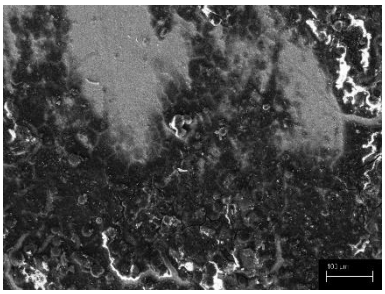
Höhe 0.3 cm

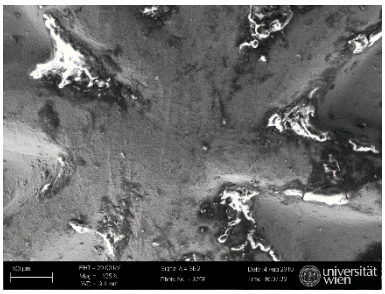
Beschreibung:

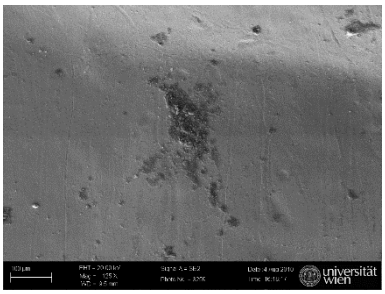
Schlagworte: Kupfer, vergoldet

Digitalverweise:

REM, EDX (Zeiss Supra 55 VP, Universität Wien)

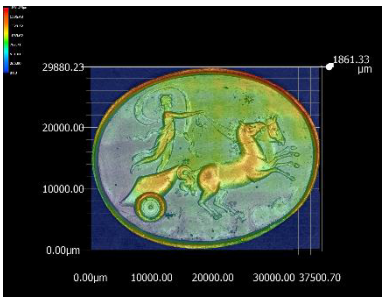






Element	Atomic%	Element	Atomic%	Element	Atomic%	Element	Atomic%
C	61,89	C	69,23	C	65,97	C	55,35
O	13,28	O	25,88	O	19,52	O	12,21
Cu	18,74	Na	0,26	Cu	12,26	S	1,35
Au	6,09	Si	0,12	Zn	0,66	Cl	0,16
		S	0,34	Au	1,6	K	0,22
		Cl	0,1			Ca	0,2
		K	0,11			Cu	6,58
		Ca	0,08			Au	0,42
		Cu	0,13				
		Zn	0,11				
		Au	1,09				

Lichtmikroskopaufnahmen (z-Scans; Keyence, VHX-5000), Universität für Bodenkultur Wien



Inventarnr.: 83939/72 **Alte Inventarnr.:** MdA4, 294

Sammlungsgr.: 530 Metallbearbeitung

akt. Standort: Standorte-TMW/TMW-Museum/E5/3-102

Titel: Galvanoplastisch erzeugtes Medaillon

Hersteller_in: Theyer, Franz; Waidele, Erwin

Ort: Wien

Datierung: 1840 **bis** 1845

Maße:

Breite 3.2 cm

Tiefe 3.7 cm

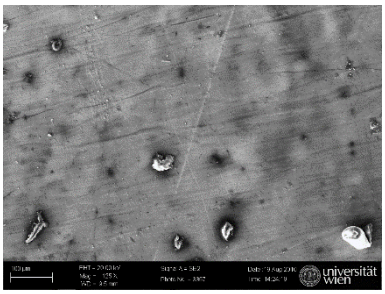
Höhe 0.3 cm

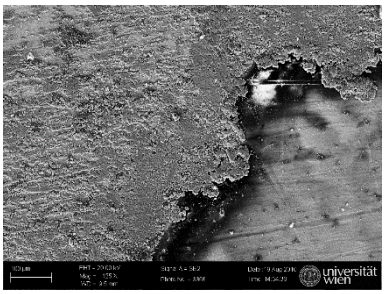
Beschreibung:

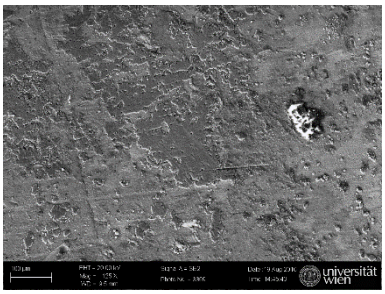
Schlagworte: Kupfer, versilbert

Digitalverweise:

REM, EDX (Zeiss Supra 55 VP, Universität Wien)

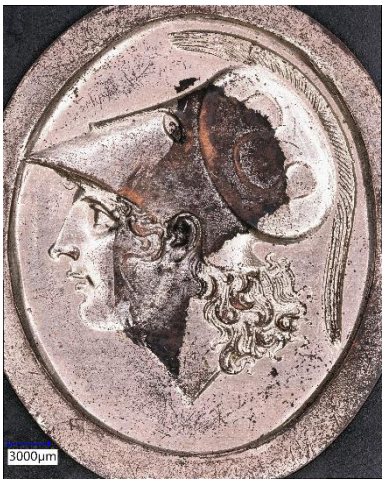


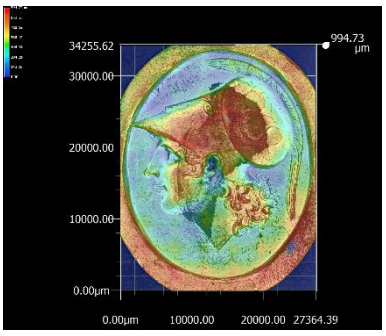


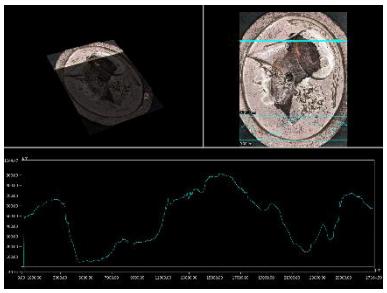


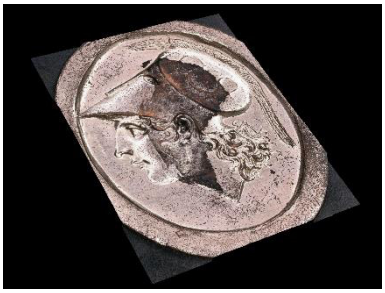
Element	Atomic%	Atomic%	Atomic%	Atomic%	Atomic%	Atomic%	Atomic%
C	71,48	49,92	67,42	57,99	70,38	42,58	45,1
O	22,09	41,7	25,36	25,73	24,72	25,53	19,82
Si		0,67		0,37			
S		3,46	0,19	1,46		11,47	7,91
Cl							0,5
Fe				0,28			
Ca		0,46					
Fe		0,41					
Cu	4,13	3,19	4,84	12,7	2,4	17,82	24,64
Ag	2,3	0,19	2,19	1,46	2,5	2,6	2,03

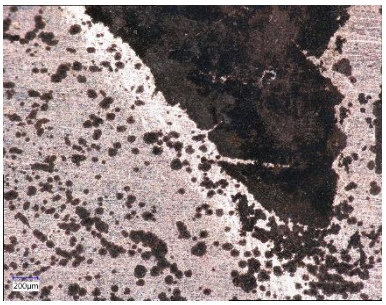
Lichtmikroskopaufnahmen (z-Scans; Keyence, VHX-5000), Universität für Bodenkultur Wien











Inventarnr.: 83939/73 **Alte Inventarnr.:** MdA4, 297

Sammlungsgr.: 530 Metallbearbeitung

akt. Standort: Standorte-TMW/TMW-Museum/E5/3-102

Titel: Galvanoplastisch erzeugtes Medaillon

Hersteller_in: Theyer, Franz

Ort: Wien

Datierung: 1840 **bis** 1845

Maße:

Breite 2.6 cm

Tiefe 3.2 cm

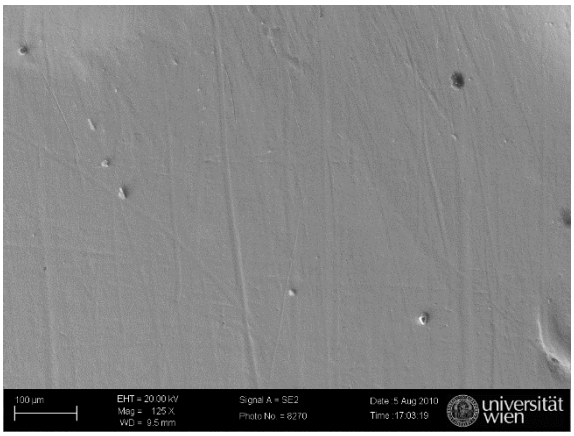
Höhe 0.5 cm

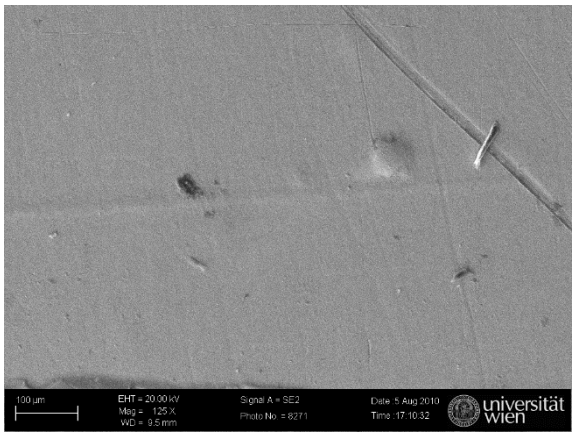
Beschreibung:

Schlagworte: Kupfer, vergoldet

Digitalverweise:

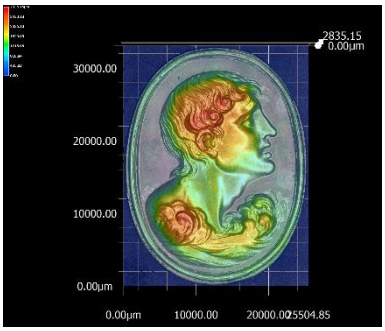
REM, EDX (Zeiss Supra 55 VP, Universität Wien)

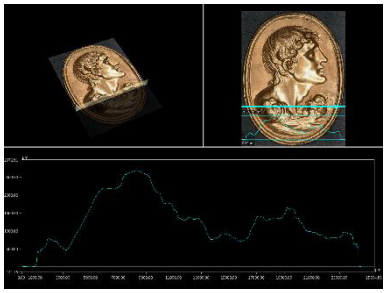




Element	Atomic%	Element	Atomic%
C	48,42	C	52,97
O	10,78	O	11,44
Cu	7,99	Na	0,72
Au	31,87	K	0,78
Hg	0,93	Ca	0,16
		Cu	1,88
		Au	7,19
		Hg	0,3

Lichtmikroskopaufnahmen (z-Scans; Keyence, VHX-5000), Universität für Bodenkultur Wien





Inventarnr.: 83939/74 **Alte Inventarnr.:** MdA4, 48

Sammlungsgr.: 530 Metallbearbeitung

akt. Standort: Standorte-TMW/TMW-Museum/E5/3-102

Titel: Fotogalvanographie

Hersteller_in: Pretsch, Paul, Bisson frères

Ort:

Datierung: 1852 **bis** 1864

Maße:

Breite 31.7 cm

Tiefe 46.2 cm

Höhe 0.2 cm

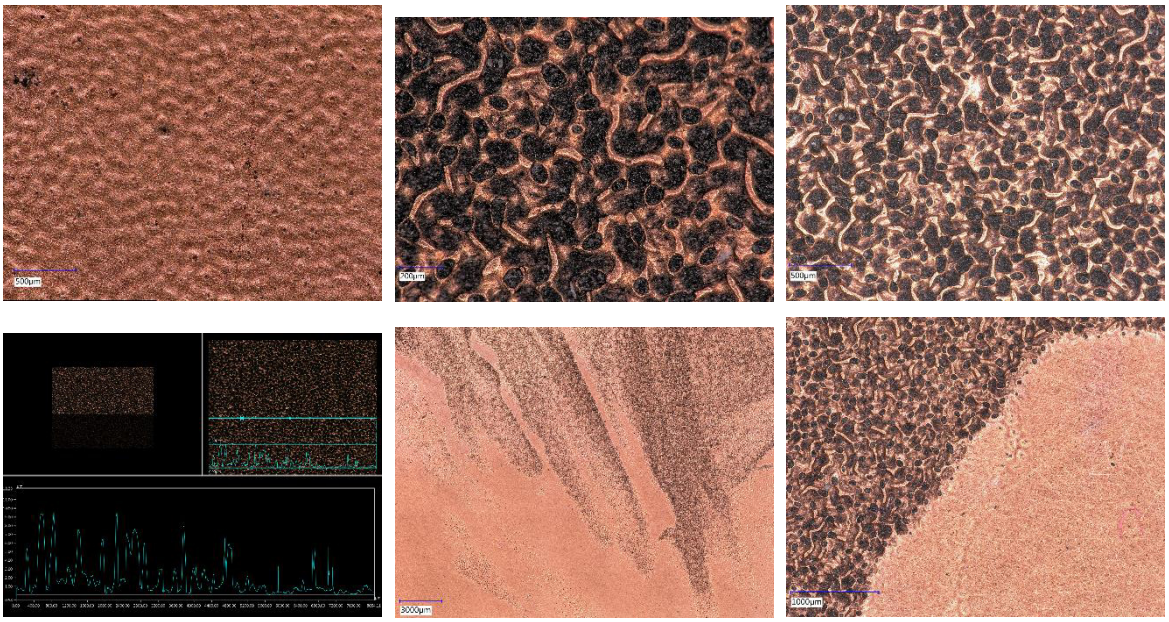
Beschreibung:

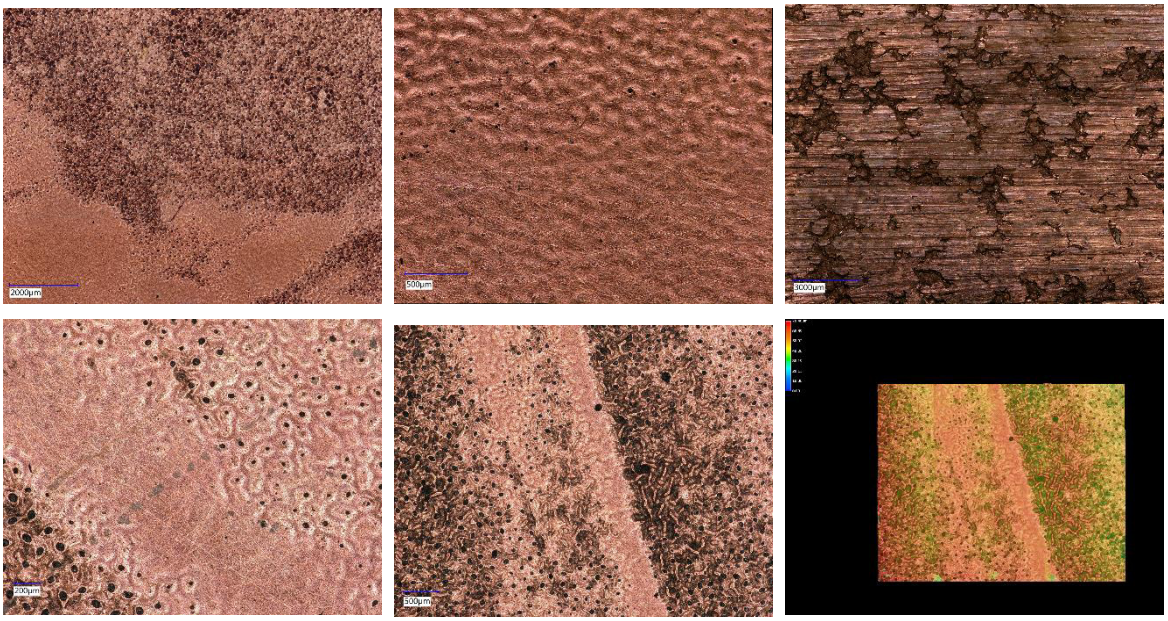
Befindet sich in Lade 4 (von oben gezählt) unter der mit schwarzem Stoff bespannten Tafel (dort befinden sich die Nummern 219-226, 228-235 und darunter 48).

Schlagworte: Kupfer

Digitalverweise:

Lichtmikroskopaufnahmen (z-Scans; Keyence, VHX-5000), Universität für Bodenkultur Wien

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Druck auf Papier (TMW Archiv)

Inventarnr.: 84183/1 **Alte Inventarnr.:** TH34675

Sammlungsgr.: 360 Satz und Druck

akt. Standort: Standorte-TMW/TMW-Museum/E5/3-102

Objektbez.: Druckplatte

Titel: Druckplatte Hl. Joseph

Hersteller_in: Theyer, Franz; Waidele, Erwin

Ort: Wien

Datierung: 1844 **bis** 1844

Maße:

Breite 22.4 cm

Tiefe 30.9 cm

Höhe 0.1 cm

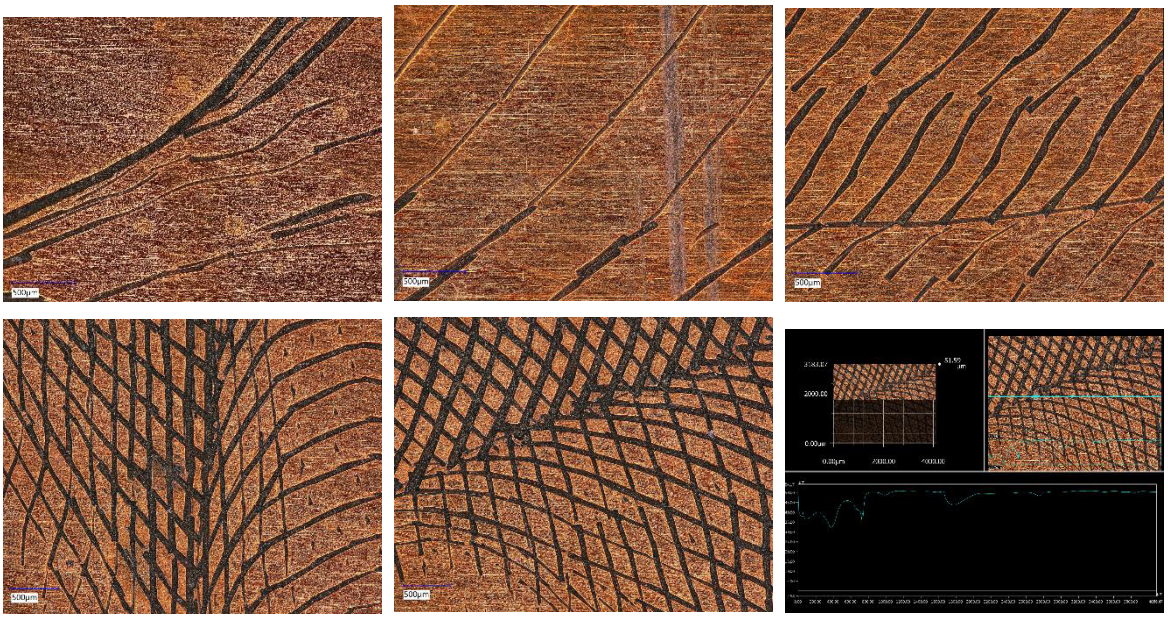
Beschreibung:

eingeschlagen in Papier bez.: "Der hl. Joseph nach Führich gest. von Beyer, Reliefplatte"

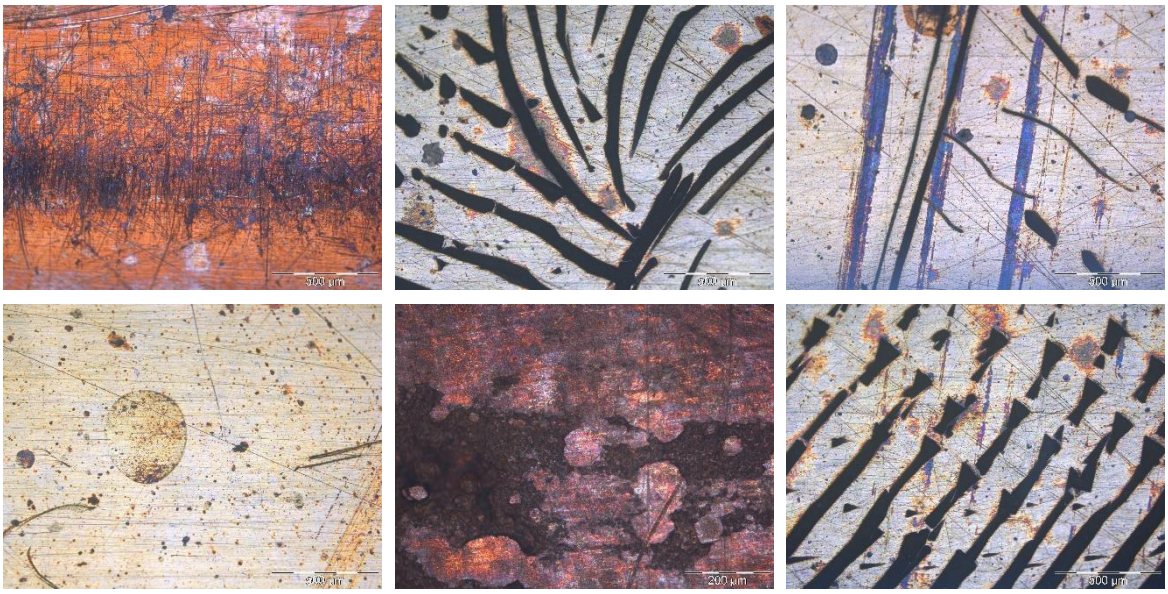
Schlagworte: Kupfer

Digitalverweise:

Lichtmikroskopaufnahmen (z-Scans; Keyence, VHX-5000), Universität für Bodenkultur Wien



Lichtmikroskopaufnahmen (Olympus GX51, Happy Platting GmbH, Wiener Neustadt)



Multispektralkamera, Rumänien

Druck auf Papier (TMW Archiv)

Inventarnr.: 84183/2 **Alte Inventarnr.:** TH34675

Sammlungsgr.: 360 Satz und Druck

akt. Standort: Standorte-TMW/TMW-Museum/E5/3-102

Objektbez.: Druckplatte

Titel: Druckplatte Hl. Joseph

Hersteller_in: Theyer, Franz, Waidele, Erwin

Ort: Wien

Datierung: 1844 **bis** 1844

Maße:

Breite 22.4 cm

Tiefe 30.9 cm

Höhe 0.1 cm

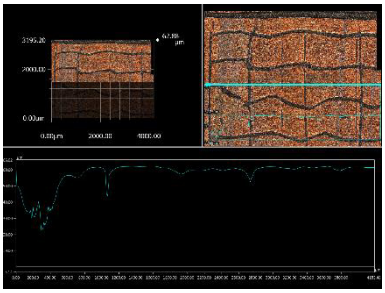
Beschreibung:

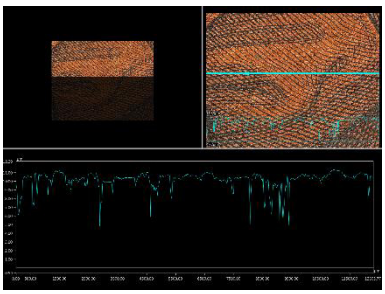
eingeschlagen in Papier bez.: "Druckplatte der hl. Josef - gestoch. v. Beyer. Mit der Aufschrift: aus Theyers Laborat 844 den 27 April 40 Druck"

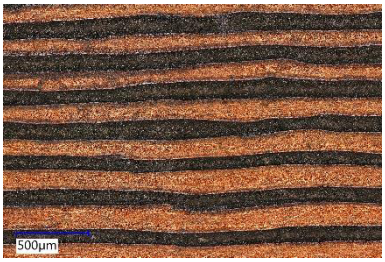
Schlagworte: Kupfer

Digitalverweise:

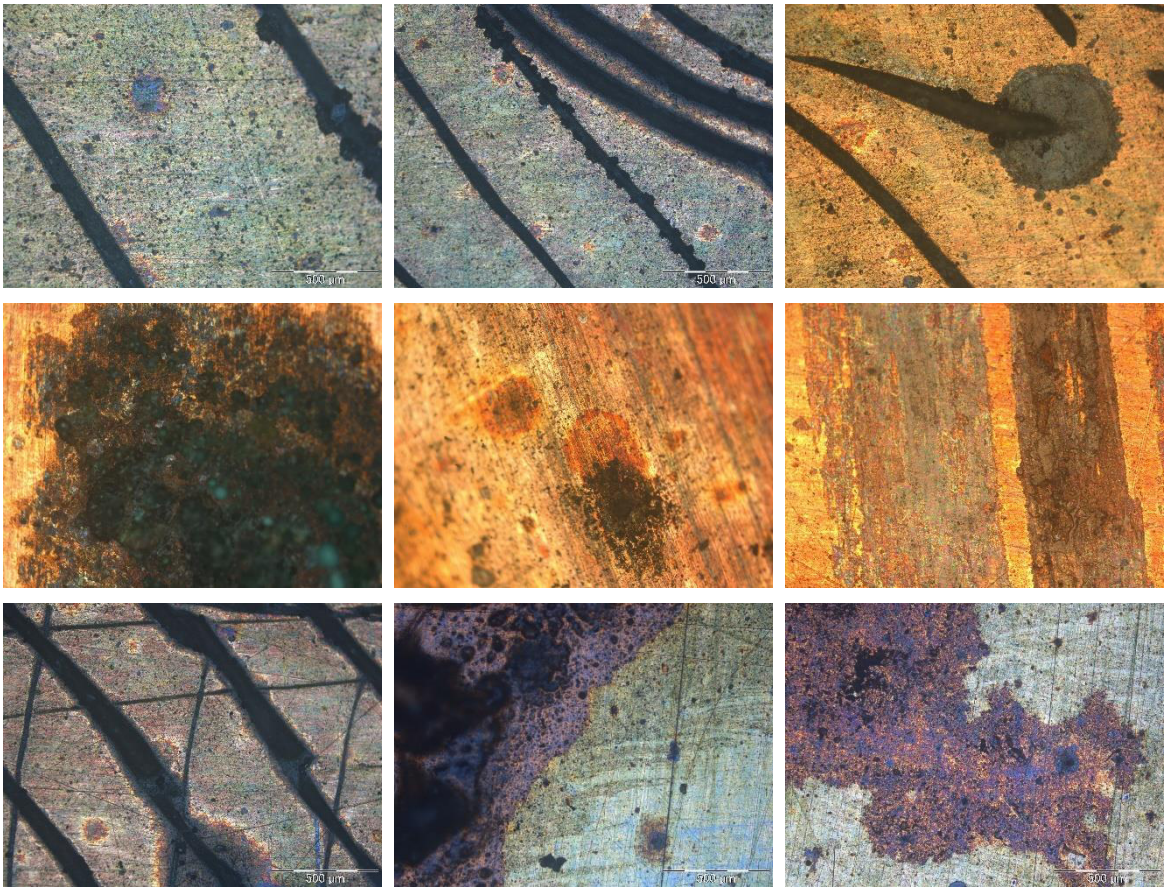
Lichtmikroskopaufnahmen (z-Scans; Keyence, VHX-5000), Universität für Bodenkultur Wien





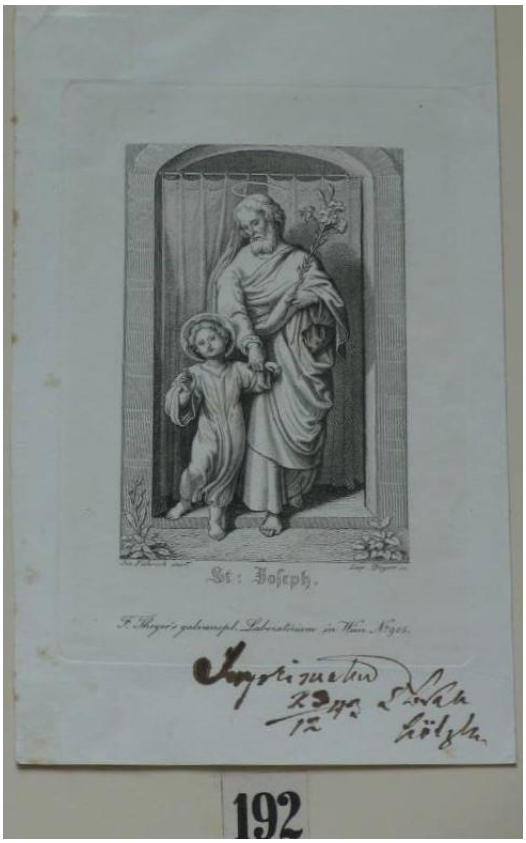


Lichtmikroskopaufnahmen (Olympus GX51, Happy Platting GmbH, Wiener Neustadt)



Multispektralkamera, Rumänien

Druck auf Papier (TMW Archiv)



Inventarnr.: 84183/3 **Alte Inventarnr.:** TH34675

Sammlungsgr.: 360 Satz und Druck

akt. Standort: Standorte-TMW/TMW-Museum/E5/3-102

Objektbez.: Druckplatte

Titel: Druckplatte Hl. Joseph

Hersteller_in: Theyer, Franz; Waidele, Erwin

Ort: Wien

Datierung: 1844 **bis** 1844

Maße:

Breite 22.5 cm

Tiefe 29.8 cm

Höhe 0.2 cm

Beschreibung:

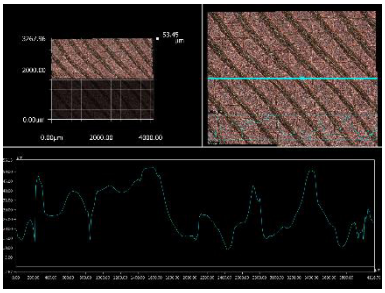
Bez.: St. Joseph, der du auf Erden den Herrn der Herrschenden Dir unterthänig gesehen hast, bitte für uns!

bzw.: Jos. Führich m.v. Leop. Beyer sculpt.

Schlagworte: Kupfer, versilbert

Digitalverweise:

Lichtmikroskopaufnahmen (z-Scans; Keyence, VHX-5000), Universität für Bodenkultur Wien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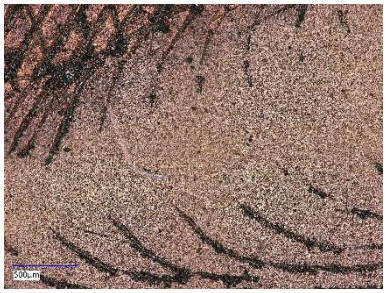
0.00µm
2000.00
4000.00

500µm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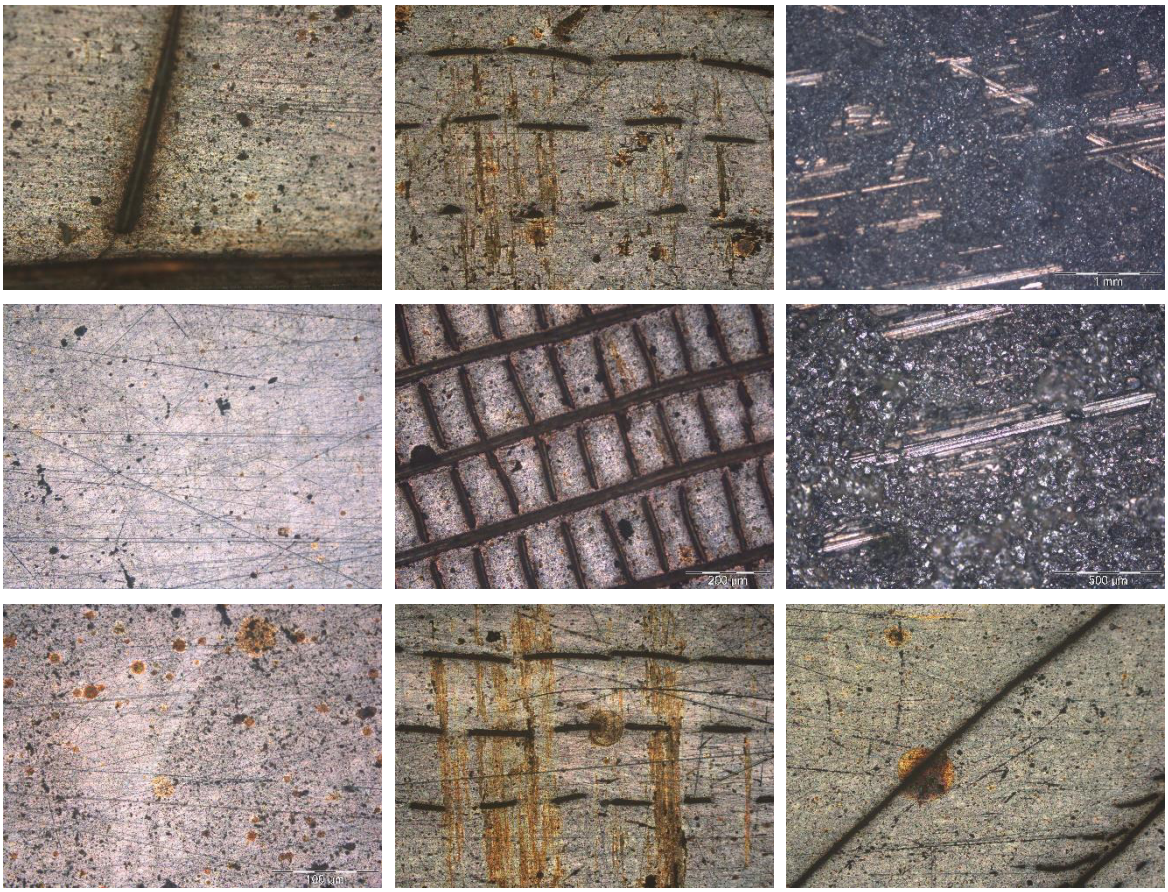
Lichtmikroskopaufnahmen (Olympus GX51, Happy Platting GmbH, Wiener Neustadt)



Appendix III

Scientific CV

Personal information

Valentina Ljubić Tobisch

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https://www.researchgate.net/profile/Valentina_Ljubic_Tobisch3

https://univie.academia.edu/ValentinaLjubic

ORCID: 0000-0002-0881-3263

Date of birth: July 15, 1978

Nationality: Croatia

Professional Experience

2017 – present	**Freelance conservator and consultant, Austria & Croatia**
	Heritage science as well as museological and preventive conservation tasks
09/2005 – 05/2017	**Museum of Technology, Vienna, Austria /** Department for Conservation and Restoration
	Position: **Head of department**
03/2010 – 09/2013	**Art Academy Split, Split, Croatia** / Department for Conservation-Restoration / conservation-restoration of metal
	Position: **Assistant Lecturer**

03/2003 – 08/2005	**Museum of Technology, Vienna, Austria /** Department for Conservation and Restoration Position: **Conservator**
2004	**Federal Monuments Authority Austria /** Department for Conservation of Archaeological Finds Position: **Freelance conservator**
1998 – 2002	**University of Applied Arts Vienna, Austria /** Department for Archaeometry Position: **Laboratory assistant**
1997 – 2002	**Part-time student job** in Elisabeth Krebs's private studio for metal conservation

Education

2010 – present	**University of Vienna /** Department of Physical Chemistry
10/1997 – 06/2002	**University of Applied Arts, Vienna, Austria /** Institute of Conservation and Restoration

Professional Award

In 2013 my colleague Martina Wetzenkircher and I were honoured with the scientific award TÜV Austria for developing the strategy for treating asbestos-containing museum objects.

Conference presentation (within the framework of the dissertaiton)

- V. Ljubić Tobisch, W. Kautek
  Heritage Science Days, 2017

  Heritage science aspects of early Austrian electrotype artefacts

- V. Ljubić Tobisch, W. Kautek
  IIC, 2019

  High photosensitivity daguerreotypes and their reproduction: physico-chemical elucidation of innovative processes developed around 1840 in Vienna

Posters

- V. Ljubić Tobisch, I. M. Corteab, L. Ratoiub, R. Rãdvanb, W Kautek
  Österreichische Chemietage, 2019
  Physical-chemical characterization of the electrodeposited printing plates from the early 1840 in Vienna
- V. Ljubić Tobisch, A. Selimović, A. Artaker, M. Klobassa, W. Kautek
  Österreichische Chemietage, 2019
  Electrotyping in Nature Printing: physico-chemical reconstruction of a cutting edge technology of the 1840s
- A. Selimović, V. Ljubić Tobisch, W. Kautek
  1st Heritage Science Austria Meeting, 2019
  Tarnishing processes on silver: Influence of the surface working method on the sulphidation
- V. Ljubić Tobisch, I. M. Corteab, L. Ratoiub, R. Rãdvanb, W Kautek
  1st Heritage Science Austria Meeting, 2019
  Physical-chemical characterization of the electrodeposited printing plates from the early 1840 in Vienna
- V. Ljubić Tobisch, A. Selimović, A. Artaker, M. Klobassa, W. Kautek
  1st Heritage Science Austria Meeting, 2019
  Electrotyping in Nature Printing: physico-chemical reconstruction of a cutting edge technology of the 1840s
- L. Nurse, V. Ljubić Tobisch
  1st Heritage Science Austria Meeting, 2019
  Conservation treatment of two leather-covered boxes, associated with the silver vessels, made by the Nürnberg goldsmith Peter Kuster, c. 1550
- V. Ljubić Tobisch, I. M. Corteab, L. Ratoiub, R. Rãdvanb, W Kautek
  TECHNART, 2019
  Physical-chemical characterization of the electrodeposited printing plates from the early 1840 in Vienna
- A. Selimović, V. Ljubić Tobisch, W. Kautek
  ISSIS, 2018

Electrochemistry in Heritage Science: Targeted Cleaning of Silver Tarnish with an Electrolytic Pencil

- V. Ljubić Tobisch, W. Kautek
  ISSIS, 2018
  Early Austrian Electrotype Artefacts
- V. Ljubić Tobisch, M. Wetzenkircher
  Heritage Science Days, 2017
  Out of sight, out of mind. The hidden hazards of historic materials – experiences and strategies at the Vienna Technical Museum
- A. Selimović, V. Ljubić Tobisch, W. Kautek
  Heritage Science Days, 2017
  Electrochemistry in conservation science: Reduction of silver tarnish with an electrochemical pencil
- T. Nagy, U. Pacher, O. Armbruster, V. Fosodeder, V. Ljubić, W. Kautek
  Bunsentagung, 2012
  Depth profiling of noble metal coatings on copper by laser-induced plasma spectroscopy
- V. Ljubić, W. Kautek
  IIC Congress, 2012
  A Perfect Copy: Analysis of the Earliest Electrotype Artefacts
- S. Arif, V. Ljubić, O. Armbruster, A. Giesriegl, T. Nagy, W. Kautek
  E-MRS Spring meeting, 2012
  Laser Cleaning of Polymeric Materials
- V. Ljubić, W. Kautek
  LACONA 9, 2011
  Diagnostics of Earliest Galvanoplastic Artefacts
- S. Arif, M. Forster, V. Ljubić, T. Nagy, U. Pacher, S. Batishche, S. Bushuk, A. Kouzmouk, H. Tatur, W. Kautek
  LACONA 9, 2011
  Particulate Laser Removal from Artefacts
- S. Arif, V. Ljubić, W. Kautek
  LACONA 9, 2011
  Laser Cleaning of Polymeric Materials

Appendix IV

Copies of published papers

Ljubić Tobisch *et al. Herit Sci* (2019) 7:20
https://doi.org/10.1186/s40494-019-0263-0

Heritage Science

RESEARCH ARTICLE Open Access

Duplication of uniqueness: electrotyping in nature printing and its application in contemporary art

Valentina Ljubić Tobisch[1*], Albina Selimović[1], Anna Artaker[2*], Martin Klobassa[3] and Wolfgang Kautek[1*]

Abstract

The nature printing technique was designed for the electrotyping reproduction of leaves and other natural products. Authentic impressions could be performed by inserting leaves between two lead plates or pressing leaves into the lead plate by a press. The impression obtained in the soft lead plate could then be further reproduced by copper electroplating. Electrochemically deposited copper is hard-wearing and therefore very suitable for the production of printing plates. However, depending on the technical implementation and the choice of the materials used, decisive differences in the faithfulness of reproductions of original motifs may occur during the electrochemical deposition. A central topic in electroforming of printing plates is the choice of the conductive layer on the mould. In the present study, it has been shown that graphite powder represents a conductive phase on the siloxane mould superior to silver and copper powder. The grain size of the copper electrodeposit depended on the powder grain size. The copper plate deposited on graphite powder showed the lowest grain size (5–20 µm) and the highest homogeneity of the print background. Hand polishing of the printing plate resulted in a much better faithfulness of the motif details than that of the machine polished version. However, the background of the print derived from the machine polished plate was the most homogeneous. Electrochemical investigation showed that remnants of the silver powder could result in local elements that could enhance corrosion and thus impair the durability of the printing plates. This phenomenon was negligible with the conductive layers consisting of graphite and copper.

Keywords: Nature printing, Printing plates, Electrotyping, Conductive layer, Heritage science, Contemporary art

Introduction

History of nature printing

A nature print is a print in which an object taken from nature serves as a printing block. They are produced by the direct use of e.g. plants or animal objects—without interaction or artistic interpretation. Nature printing was developed in the Middle Ages to support the collections of medicinal plants in parallel to the botanical tradition of the production of herbaria. The durability of herbaria being limited, botanists started to soak the dried and pressed plants in ink to print them on paper. The first impressions of leaves and fruits obtained were very simple. The earliest dateable nature print dates to 1228. By the seventeenth and eighteenth century, nature printing had developed into a serious scientific method of plant reproduction. Nature printing was also popular in Asia, namely in Polynesia, China and Japan, where prints of fish and other sea species are still being produced [1, 2].

Historic herbal books describe that both sides of the plant were usually ink-coated [3]. The plant was then placed between two sheets of paper and pressure was applied to achieve a true-to-the-original imprint. This process could be repeated up to two more times without requiring a renewed soaking of the object in additional ink. Usually six prints could be obtained using the same plant. While the first two prints generally turned out

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rather dark, the subsequent two prints were the most faithful duplicates. The last two prints often had to be coloured once they had dried out, while the truest second ones were left uncoloured. In the sixteenth century, several European botanists knew of and applied the technique which was known as *ectypa* or *typographia plantarum* at the time [2, 3].

The first step in the process of nature printing, the technique developed and patented by Alois Auer and the Austrian National Printing Office (k. k. Hof- und Staatsdruckerei) in 1852 [4] was the creation of an original imprint of the object in lead by means of a printing press. From this original imprint, a copper intaglio printing plate was produced using the process of galvanoplasty or electrotyping, which was a cutting edge technology at the time [5]. The time-consuming electrotyping process was employed twice. First a positive of the imprinted plant was made from the negative impression in lead [6]. This positive served as a matrix for a second plate produced in a galvanic copper bath, which was identical to the initial imprint in lead, but suitable as a printing plate. When the quality of the copper printing plate started to deteriorate a new one could be produced from the matrix. In principle, the process enabled a theoretically endless print run, although in practice the laboriousness involved prevented large editions [7, 8].

This technique allowed the production of printing plates from dried plants, fabrics, lace samples, embroideries and other originals. It enabled the production of impressions "identical to the original", in Auer's words, both in white colour on dyed ground and in natural colours on white paper, even with the use of delicate embossments and recesses. Two examples are represented in Fig. 1. If we consider the touch of the plant that leaves an imprint a unique and irretrievable moment, then the Viennese technique of nature printing enables the paradoxical duplication of uniqueness. The main motive for the development and perfection of this printing technique by the Austrian National Printing Office was the possibility of its application in the production of large editions and its interest in duplicating processes.

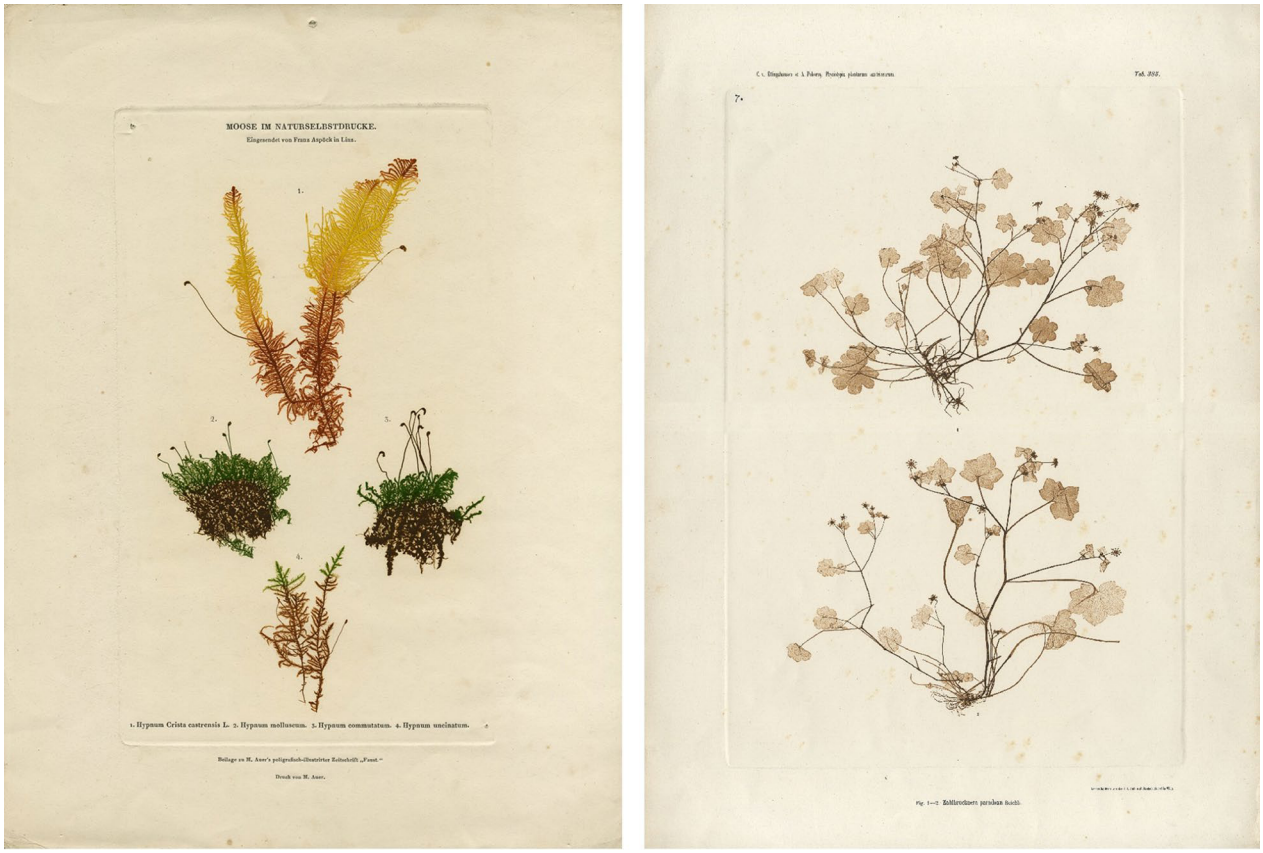

Fig. 1 Left: nature print of spondulicks, 1854, Franz Aspöck, (M. Auer, Faust, Poligrafisch-illustrirte Zeitschrift, 1854, Vienna) © Technisches Museum Wien. Right: nature print of Zahlbrucknera, Ettingshausen & Pokorny, k.k. Hof- und Staatsdruckerei, 1856, Vienna, © Technisches Museum Wien

Contemporary attempt to recreate the historic technique

One of the authors, the artist Anna Artaker combines her interest in the history of photography and William Henry Fox Talbot's earliest botanical photograms with a revival of the historical technique of nature printing. She presented a series of contemporary nature prints entitled "The Pencil of Nature" at the Bank Austria Kunstforum in Vienna, Austria, in 2017 [9]. If nature is defined as encompassing all phenomena that occur without human intervention, is it possible to reproduce them without changes? Considering that the touch of the plant leaves an impression of a unique and irretrievable moment, the Viennese technique of natural self-printing allows the paradoxical doubling of uniqueness.

While trying to reconstruct the nature printing technique of Alois Auer, questions and problems concerning the surface quality of the produced prints arose. A graininess in the plate background was observed that should appear as smooth and flawless as possible to bring the motif to the foreground. The resulting print exhibits its own base tone originating from the graininess of the matrix (Fig. 2).

Electrochemical deposition was used fairly quickly after its discovery at the end of the 1830s both for artistic and multiplication purposes [5]. If the matrix material was not electrically conductive, a coating process with an electrically conductive material was necessary. This was achieved either by the application of electrically conductive powders or by electroless metal deposition [10]. The main requirement for the conductive layers is that it generates a thin film imperceptible enough, so that it does not impair the shape or the details of the motifs to be replicated. The cheapest and most commonly used method in historic techniques was graphitizing. Apart from finest graphite powder, metal powders such as silver, copper or even gold powder were used [11–13].

The present investigations intended to provide information on the electrical conductivity of graphite, silver and copper powders on the one hand and on the quality and roughness of the electroplated surface on the other hand [14]. The experiments allowed to identify the optimum electrode material for the most ideal moulding and showed whether parts of the conductive layer were transferred to the electroformed positive.

Electrochemical methods of analysis play an increasingly important role in conservation science [15, 16]. Particularly advantageous is the fact that they are practically non-destructive methods. In fact, most electrochemical methods of analysis can be performed directly on the object without the necessity of sampling. The size and shape of the object do not play a major role since the electrochemical methods are transportable and can be applied in situ. They can be used to evaluate the protective properties of coatings on metal surfaces in the field of heritage science [17]. Besides the use of electrochemical methods in the analysis of metal objects, the electrolytic reduction of tarnish layers on metals is an established method of intervention in the restoration of metal artefacts [15].

The main task of this study was a comparison of three conductive layers which have historically been used in the electrochemical deposition of copper. Conductive layers are believed to play an important role in the faithful reproduction of such impressions. A considerable amount of research has been invested in the historical studies of natural self-printing technology, but no known study has yet focused on the microscopic surface of the printing plates. Moreover, cyclic voltammetry was employed to identify the components of the surface

Fig. 2 Photographs of the lead plate onto which the plant was impressed (left), of the copper plate, the positive (middle), of the print on paper (right). © Anna Artaker

layers and their corrosion stability on the produced copper plates as well as the effects of various surface polishing treatments after the electrotyping process.

Experimental

Production of electrotype samples started with the impressing of plant motives onto a 3 mm thick lead plate. A negative of this plate was produced using a two-component siloxane (MM 240 RTV, Bodo Möller Chemie Austria GmbH) and was mounted on a stable support plate of acrylic glass. One-third of the siloxane surface was coated with copper powder (Gold Bronze Powder, Eckart-Werke, Germany), the second third with graphite powder (Graphite Fine Powder extra pure, Merck, Austria) and the last third was coated with silver powder (Silver Powder 1000/1000, Ögussa, Austria). The metal powders exhibited platelet morphologies resulting from their electrolytic production. All three powders were used as received by the manufacturer. They were first applied with a soft brush and then smoothed into the siloxane surface with fingers. The excess was removed with compressed air. The application of the conductive powders were originally carried out with a long-haired brush [10]. The brush was dipped into the conductive powder and led in circular movements over the negative mould until the whole surface showed a metallic shine.

The conductive layers on the siloxane mould were electrically contacted by an insulated copper wire (Fig. 3a). This wire also served as a mechanical suspension device in order to hold the acrylic base and the mould in the electrolytic bath. An additional contact silver lacquer electrode was applied along the circumference of the sample (Fig. 3b). The space between the acrylic glass plate and the siloxane mould was sealed with liquid wax to prevent the electrolyte from penetrating in between.

This sample was submersed into a sulphuric acid thick-film copper bath (Bright Copper ACG 8, Schlötter Galvanotechnik) at 20 °C (Table 1). This acid copper electrolyte contains a single additive not disclosed by the manufacturer. The plated deposit has a high deposition rate, very low internal stress and is soft which makes polishing very easy. The bath was kept in constant motion by a pump. A DC-power supply (Heraeus, 10 V, 100A) served as current source for the electrolysis. The copper anodes (200 × 400 mm, 1 cm thick) were enclosed by polypropylene anode bags. A voltage of 0.5 V was applied until the entire sample surface was covered. Then, it was increased to 2 V. After 4 h, the negative plate (working electrode) was rotated by 180° and the electrolysis was continued another 4 h. After this electrodeposition process, the deposited copper plate (Fig. 3c) was separated from the underlying mould with a blunt knife which was inserted between the siloxane negative and the copper positive. The copper plate was rinsed with water and buffed with a soft brass wire brush, as described in the historical reports [11–13].

Table 1 Galvanic bath "Glanzkupferbad ACG 8"

Parameter	Information provided by manufacturer
Cu concentration	39.0 gl^{-1}
H_2SO_4 concentration	97.8 gl^{-1}
Cl^- concentration	58.0 g^{-1}
Fe concentration	0.1 gl^{-1}

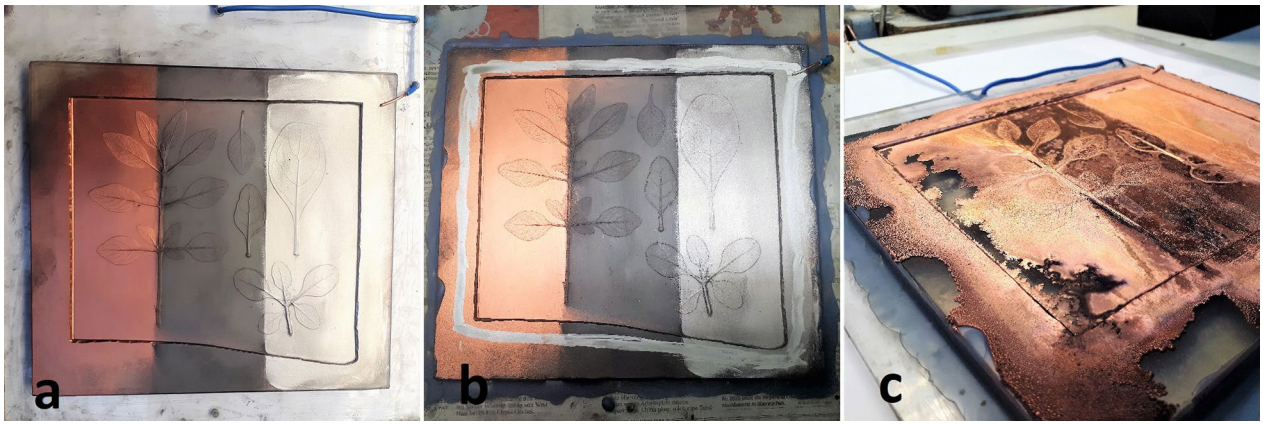

Fig. 3 Siloxane mould. **a** Left section coated with Gold Bronze Powder 9900 Copper; middle section coated with Graphite Fine Powder extra pure; right section coated with Silver Powder 1000/1000. **b** Powder coated sample with additional contact silver lacquer electrode and with wax seal to prevent electrolyte penetration. **c** Electrodeposited copper layers

Polishing of the galvanic copper printing plates has been an established finishing step. Mechanical polishing of the buffed and brushed sample removed various roughnesses on the surface by pressing and rubbing so that the individual asperities were eliminated until the surface appeared mirror-smooth. Historically, various tools have been used, namely polishing steel, agate, some types of horn and bloodstone/hematite [12]. Thin galvanic layers were often polished with leather which was coated with a mixture of oil and a hard powder such as pumice stone, tin ash or bloodstone. Later, galvanic objects were polished on the polishing machine with a rotating brush or fabric disc.

It is not clear how Alois Auer polished the obtained printing plates for the production of nature prints. Therefore, in the present work, three surface states were examined. The plate segments, made conductive with silver, graphite and copper powder respectively, were sawn into three segments so that each contained one-third of each powder type. One-third was polished manually using bloodstone while the second third was polished with a fabric disc on a polishing machine and the last third remained untreated (compare Fig. 6 below). A polishing paste was used with a rotating fabric disc (Baier's Enkel Nfg., Silberglanz-Paste, fat-bound).

Measuring windows of ca. 1 cm^2 serving as working electrode surfaces were generated on each plate segments by an electrically insulating siloxane adhesive (Saint-Gobain Performance Plastics MG Silicon GmbH, SK 6000 Neutral). Electrochemical measurements were carried out with an Ag/AgCl reference electrode (RE, + 0.222 V vs. SHE [18] and a gold counter electrode in the form of a wire spiral (CE) in a glass tube with a porous frit as electrolyte junction. The cyclic voltammetry and the open circuit transient measurements were performed with an electrochemical workstation (CH Instruments, 760C). A 0.1 M K_2CO_3 (pH = 10.6) solution with deionized water (Milli-Q) served as electrolyte. The pH value was determined by a glass membrane electrode (Metrohm, 780 pH Meter). Before starting the electrochemical measurements, the plate was degreased inside the measuring window by wiping with a cotton swab soaked with acetone.

Optical micrographs were recorded with a digital microscope (Keyence, VHX-5000). Electron micrographs were registered with an environmental scanning electron microscope (FEI, Quanta 250 FEG with a Schottky field emission source).

Results and discussion

The metal powders applied on the insulating siloxane moulds constitute the conductive electrodes for the electrodeposition of the copper layers. The morphology, the volume resistivity, and the thickness of the applied metal powders should have an influence on the quality of the electrotypes.

The local current density affects the deposit morphology [19]. It is proportional to the reciprocal of the volume resistivity and the thickness of the applied powder layer at an applied constant potential:

$$j \propto 1/R \propto 1/\rho \times d \quad (1)$$

with the powder layer thickness d, resistance R, and the volume resistivity ρ (Eq. 1). The respective ρ are represented in Table 2. ρ of graphite exhibits the highest value in respect to Cu and Ag. The powder grain sizes and the Cu deposit grain sizes were evaluated by scanning electron microscope (SEM; Fig. 4) and optical microscopy, respectively. According to Eq. 1, graphite should exhibit the lowest local current density at a $d \approx 50$ µm. The lower the current density the higher the contribution of the base reproduction growth type versus the field-oriented type will be. This correlation led to a smooth and small-grained deposit for graphite (Fig. 5, Table 2).

When a base reproduction occurs at moderate inhibition intensity by an additive, the respective powder morphology can have a direct influence on the electrodeposit texture. The base electrode graphite shows the smallest grain size (< 15 µm) whereas Ag shows greater sizes (> 35 µm), and Cu a broad distribution of up to 30 µm (Figs. 4 and 5, Table 2). Therefore, the

Table 2 Conductive powder properties and electrodeposited copper plate grain sizes

Name	Volume resistivity, ρ [Ωm], 20 °C	Powder layer thickness *d* [µm]*	Powder grain size [µm]**	Cu deposit grain size [µm]*
Cu (gold bronze powder 9900)	$1543 \cdot 10^{-8}$ (18)	55.6 ± 8.4	10–30	20–50
Graphite (graphite fine powder extra pure)	$3500 \cdot 10^{-8}$ (18)	47.5 ± 7.0	1–15	5–20
Ag (silver powder 1000/1000)	$1467 \cdot 10^{-8}$ (18)	55.2 ± 17.9	35–40	20–50

* Evaluated from optical micrographs. **Evaluated from scanning electron micrographs

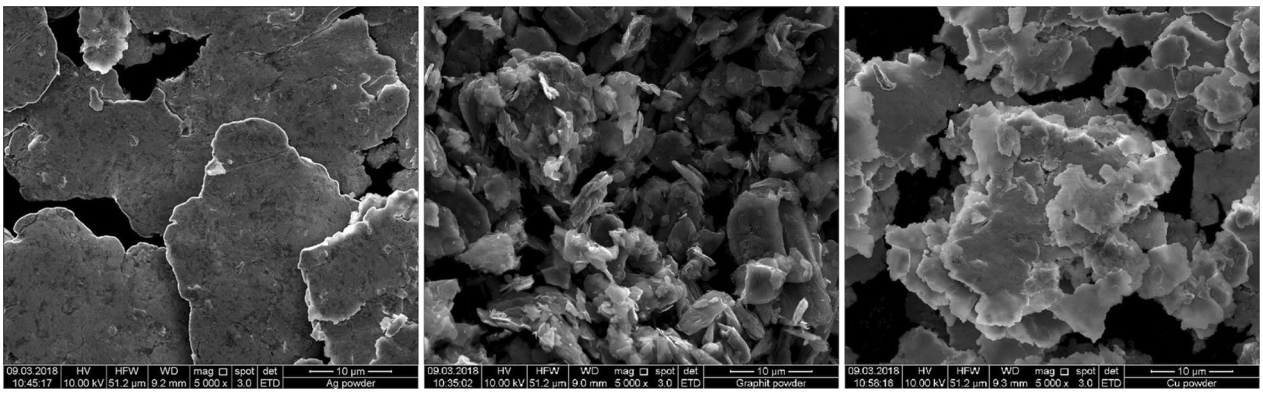

Fig. 4 Scanning electron micrographs of Silver Powder 1000/1000 (left), Graphite Fine Powder extra pure (middle) and Gold Bronze Powder 9900 Copper (right). 10 kV, ×5000

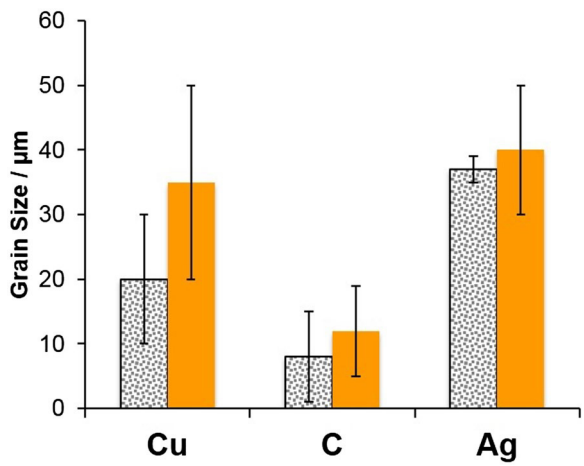

Fig. 5 Conductive powder (dotted) and electrodeposited copper plate (orange) grain sizes

observed Cu deposit grain size on graphite resulted in the lowest value (Figs. 4 and 5, Table 2).

The Cu plate electrodeposited on Cu powder was an incomplete, uneven, and inhomogeneous layer (Figs. 3c and 6). The region near the inhomogeneities were partially delaminated and exhibited darkened and "burned" surfaces. Therefore, electrolyte penetrated also between the Cu deposit and the Cu powder layer on siloxane mould. The Cu edges showed grainy and powdery morphology due to enhanced local current densities. The "burned" surface features can be correlated with high rates of hydrogen discharge [20]. This leads to a pH increase in the interface resulting in the precipitation of hydroxide or basic salts of Cu. These may be occluded by the plated deposit.

The Cu plate electrodeposited on either graphite or Ag powder provided a homogeneous and compact layer (Fig. 6). Powder remnants still adhered visibly in depressions (Fig. 7, Table 3).

The after treatment was performed by hand (stone) polishing using hematite (bloodstone) and machine polishing (rotating fabric disc). The advantages of stone polishing are the higher gloss, the texture of the surface becomes denser, and the metal loss is minimized in contrast to machine polishing. The elevated parts of the surface profile appeared dark in the machine polished regions. This is due to the specular reflection of the illumination light which cannot be collected in the microscopic objective. Fine one-directional scratches were introduced in these flat regions by the rotating fabric disc treatment. Hand polishing yielded much shinier regions without the leaf motifs than machine

Fig. 6 Photograph of the electrodeposited copper printing plate. Vertical column with various conductivity powders on siloxane. Left: Ag. Middle: graphite. Right: Cu. Horizontal rows with various post treatments. Bottom: untreated. Middle: machine polished. Top: hand polished

polishing. Practically no scratches were introduced by the hematite/bloodstone treatment. Hand polishing did not affect the depressed features of the original leaf in contrast to machine polishing. A substantial difference in quality was observed between the electroformed leaf details of the plate deposited on Ag and graphite: the faithfulness to the original was by far superior on the Cu plate deposited on the graphite base electrode than that deposited on the Ag base electrode. A Cu base electrode resulted in a rough surface. Machine and hand polishing yielded comparable qualities as the Cu plate deposited on the Ag base electrode.

The prints of the three plates separated by their polishing treatment (Fig. 6) showed drastic differences in quality (Fig. 8). The faithfulness to the original leaf motif from the hand polished plate was by far superior to that treated by machine polishing. On the other hand, the background of the print from the machine polished plate was more homogeneous than that from the hand polished. The print from the untreated plate exhibited a good faithfulness to the original leaf motif but showed strong inhomogeneities of the background.

The remnants of the conductive powder layers on the electroformed Cu printing plate introduce local elements which can accelerate localized corrosion reactions. This can yield enhanced roughness thus impairing the long-term stability and applicability of such artefacts. The faithfulness of prints would be diminished by an increased plate roughness. Also, the graininess in the plate background would be enhanced.

The corrosive behaviour was studied by cyclic voltammetry in a 0.1 M K_2CO_3 solution (pH = 10.6). The Cu oxidation to Cu(I) oxide

$$2Cu + H_2O \rightleftharpoons Cu_2O + 2H^+ + 2e^- \quad (2)$$

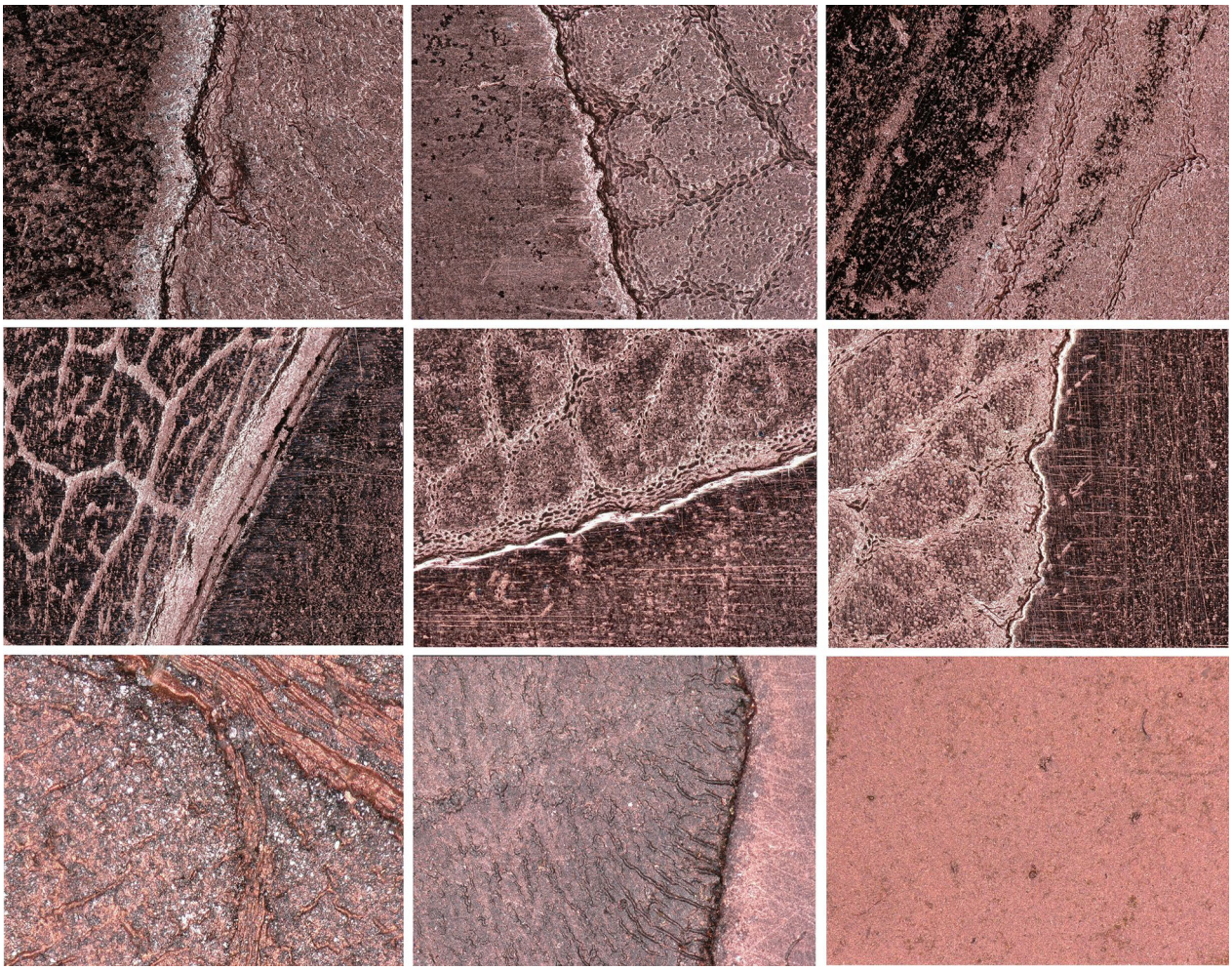

Fig. 7 Optical Micrographs of the moulded side of the electrodeposited copper printing plate. Vertical column with various conductivity powders on silicon. Left: Ag. Middle: graphite. Right: Cu. Horizontal rows with various post treatments. Bottom: untreated. Middle: machine polished. Top: hand polished

Table 3 Copper deposit characterization

Conductive layer	Untreated	Machine polished	Hand polished
Cu (gold bronze powder)	Incomplete, uneven, inhomogeneous, burned. Matt appearance	Incomplete, uneven, inhomogeneous plate. Scratches on elevations. Poor faithfulness to the original	Incomplete, uneven, inhomogeneous plate. Smoother than machine polished, no scratches. Moderate faithfulness to the original
Graphite powder	Complete, compact layer. Matt appearance Remnants of graphite powder	Scratches on elevations. Impaired faithfulness to the original	Smoother than machine polished, no scratches. Best faithfulness to the original
Ag (conductive silver powder)	Complete, compact layer. Matt appearance Remnants of Ag powder	Scratches on elevations. Poor faithfulness to the original	Smoother than machine polished, no scratches. Moderate faithfulness to the original

Fig. 8 Photograph of the print on paper derived the plate shown in Fig. 6. Vertical column with various conductivity powders on siloxane. Left: Cu. Middle: graphite. Right: Ag. Horizontal rows with various post treatments. Bottom: untreated. Middle: machine polished. Top: hand polished

and the further oxidation to Cu(II) oxide

$$Cu_2O + H_2O \rightleftharpoons 2CuO + 2H^+ + 2e^- \quad (3)$$

as well as the respective reduction reactions could be detected with remnant Ag, graphite powder, and Cu powder even after machine and hand polishing (Fig. 9). The anodic peak of the Cu_2O formation appeared at a potential positive of the Nernst equilibrium potential of this reaction $U_0 = -0.16$ V (Eq. 2, Table 4). The reduction of Cu_2O occurred as a peak between ca. -0.2 and -0.4 V. The oxidation of Cu_2O to CuO supported a broad anodic current wave at $U > +0.5$ V (Eq. 3, Table 4). The reduction of CuO yielded a peak negative of the respective Nernst equilibrium potential $U = +0.04$ V. Remnant Ag powder shows a strong redox activity and thus introduced a local element. The Ag oxidation on an untreated and a machine polished sample led to anodic peaks at $U > 0.5$ V. The first may be related to the oxidation to Ag^+

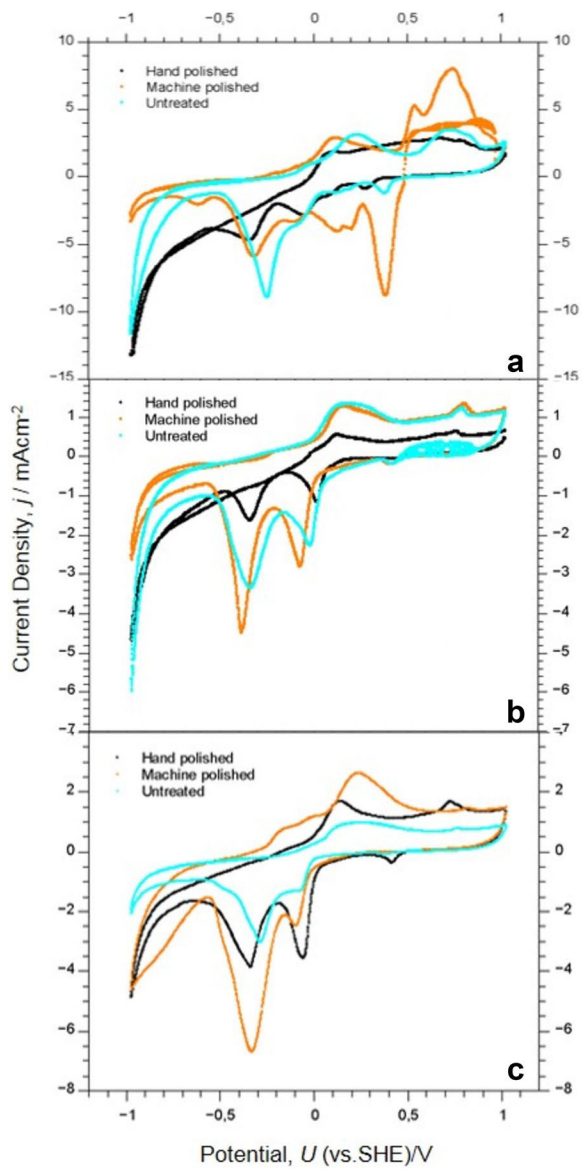

Fig. 9 Cyclic voltammograms of copper plate surface in 0.1 M K_2CO_3, pH = 10.60. Scan rate = 10 mVs^{-1}. Comparison of **a** silver, **b** graphite, **c** copper powders as conductive layers on the mould. Parameters: polishing methods

Table 4 Reactions of copper in alkaline solution (21)

Reaction	Nernst equilibrium potential vs. SHE, U_0	Nernst equilibrium potential vs. SHE, U_0 pH = 10.60
$2Cu + H_2O \rightleftharpoons Cu_2O + 2H^+ + 2e^-$	0.47–0.059 pH	−0.16
$Cu + H_2O \rightleftharpoons CuO + 2H^+ + 2e^-$	0.57–0.059 pH	−0.06
$Cu_2O + H_2O \rightleftharpoons 2CuO + 2H^+ + 2e^-$	0.67–0.059 pH	+0.04
$Ag \leftrightarrow Ag^+ \rightleftharpoons e^-$	$0.80 + 0.059 \log[Ag^+]$	~ +0.50 ([Ag*] ~ 10^{-5} M
$2Ag + H_2O \rightleftharpoons Ag_2O + 2H^+ + 2e^-$	1.17–0.059 pH	+0.54

and the second peak around +0.7 V which is positive of the Nernst equilibrium potential $U_0 = +0.54$ V is correlated with the oxidation to silver (I) oxide (Table 4).

$$2Ag + H_2O \rightleftharpoons Ag_2O + 2H^+ + 2e^-. \quad (4)$$

The reduction of Ag_2O yielded negative peaks at $U < U_0 = +0.54$ V. Machine polishing led to a strongly scratched surface resulting in an increased surface area and higher current densities. The hand polished and untreated surfaces exhibited drastically smaller redox current densities.

These results demonstrate the strong electrochemical activity of Ag powder remnants, even after polishing treatments. Therefore, a local element of this noble metal can cause the dissolution and corrosion of the Cu printing plate. It must be pointed out that hand polishing with hematite/bloodstone resulted in the lowest electrochemical activity in contrast to machine polishing.

Conclusions

The nature printing technique, originally developed in the nineteenth century, makes use of plants and other natural subjects to produce images. In the present study, synergistic effects of the cooperation between contemporary art and heritage science in the reconstruction of the historical technique of nature printing are presented. New plates for nature printing were produced using the historic process in order to gain a better understanding of the production technique. The aim was to make individual production steps comprehensible and to find practicable solutions for difficulties encountered in production. One of the main challenges was the production of electrodeposited copper printing plates usually preceded by the coating of the motif with an electrically conductive material. Three different conductive layers, copper, graphite and silver powders, were investigated in respect to their efficacy by morphological investigations using electron microscopy, optical microscopy, and cyclic voltammetry. The suitability of the electrochemically deposited printing plates could be related mainly to the various grain sizes and the electrical conductivities of the investigated conductive powders, as well as the polishing treatments. It could be confirmed that graphite is the best electrochemical conductor in the manufacture of printing plates with high faithfulness to the original motif.

Abbreviations

d: layer thickness; DC: direct current; CE: counter electrode; *j*: current density; *l*: litre; *g*: gram; NHE: normal hydrogen electrode; pH: power of hydrogen; *R*: resistance; ρ: volume resistivity; RE: reference electrode; SEM: scanning electron microscope; SHE: standard hydrogen electrode.

Authors' contributions

VLjT, AA and MK conceived the presented idea and carried out the fabrication of the galvanic plate. VLjT and AA explored the historical background of nature printing. VLjT and AS carried out the analytical experiments. VLjT, AS and WK evaluated the data and wrote the manuscript. WK supervised the project. All authors read and approved the final manuscript.

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Competing interests

The authors declare that they have no competing interests.

Availability of data and materials

All data generated or analysed during this study are included in this published article.

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Highly Photosensitive Daguerreotypes and their Reproduction: Physico-chemical Elucidation of Innovative Processes Developed Around 1840 in Vienna

Valentina Ljubić Tobisch*[a], Wolfgang Kautek *[a]

Abstract: *A physico-chemical elucidation of the world-wide first photographic technology allowing manifold reproduction is presented. An etched daguerreotype manufactured around 1840 in Vienna, preserved by the Technisches Museum Wien, served as a case-example. Surface analysis showed that the photographic process involved the formation of colloidal Ag nanoparticles (AgNPs) with sizes of 30-120nm with shell layers consisting of Ag_2O, Ag_2S, and some AgCl. The breakthrough photographic technique provided a hitherto unachieved high sensitivity due to various halogenide mixtures without Hg. The image development consisted in the reduction of the Ag halides by H_2SO_3 created by the hydrolysis of S_2Cl_2 leading to AgNPs adjacent to the latent image Ag nuclei. The fixation of the image was performed either by KCN or by $Na_2S_2O_3$. The investigated plate exhibits etched areas with Ag_2O conversion layers and no Cl or S. The first reproduction method for daguerreotypes was invented by Joseph Berres in Vienna. It consisted in etching to enable printing. He applied a gum arabic solution on the fixed image surface. The gum arabic preferentially wetted the exposed AgNP regions so that unexposed areas could be etched by HNO_3.*

Introduction

The French artist Louis Jacques Mandé Daguerre is considered the inventor of early photography[1–6]. His invention, publicly reported 1839 in Paris, marked the decisive step in the development of reproduction technology. During the preparation of the daguerreotype, a silver-plated surface was sensitized by silver iodine vapour and exposed to light in a camera. Then the plate was fumigated with mercury vapour and permanently fixed with a hot sodium thiosulfate solution[1,7–9]. At the beginning of the daguerreotype, long exposure times were a hindrance for the creation of the portraits and moving scenes like street views. On the one hand, this was due to the low light's optics available at the time, and on the other hand, to the relatively weak photosensitivity of the iodized silver surface. In order to reduce the exposure time and improve the photographic quality, further fundamental chemical and physical inventions had to be made[10].

Shortly afterwards, at the beginning of 1840is, remarkable inventions in the field of early photography have also been made in Vienna[11–17]. Josef Maximilian Petzval, a professor for mathematics, designed the very first photographic portrait objective lens (Fig. 1)[12–14,18,19]. This was the first mathematically calculated precision objective lens in the history of photography. Petzval's revolutionary dual lens exhibited a much higher luminous intensity and was more powerful than Daguerre's camera lens allowing exposure times of less than a minute. The lens was manufactured by the Viennese optician Peter Wilhelm Friedrich von Voigtländer. He developed a new camera equipped with Petzval's objective which was sold successfully worldwide.

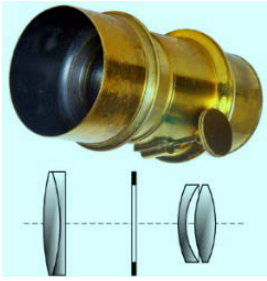

Figure 1. Petzval lens (objective). The first photographic portrait objective lens in the history of photography[18]. © Tamasflex.

Moreover, the Viennese photographic pioneers Franz Kratochwila and the medical doctors the brothers Johann and Josef Natterer developed new sensitization procedures in 1840/41 deviant from techniques applied in other countries[11–13,19] . In order to improve the poor light sensitivity of the iodized silver surface used by Daguerre, they developed sensitization procedures employing mixtures of bromine, chlorine and iodine applied in various sequences and compositions (Table 1). In this way snapshots could be taken for the first time[12]. The first two worldwide known photographs of street scenes and people crowds originate from them[3,13,14]. A representative fuming box and laboratory utensils for daguerreotype are depicted in Fig. 2a and Fig. 2b, respectively. In addition, the Natterer brothers developed another procedure omitting mercury used in common daguerreotype[12].

Figure 2 left. Fuming box for daguerreotype, Inv.Nr.: 2112, Technisches Museum Wien, Austria. **right.** Wooden box with laboratory utensils for daguerreotype, 1839 Giroux Paris, Inv.Nr.: 2110, © Technisches Museum Wien, Austria.

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Table 1. Daguerreotype processing steps reported in literature

Processing steps	Chemical reactions	
Coating the Cu plate with Ag		
Polishing		
Sensitization with I_2 (L. Daguerre 1839)[1–3,10] Multiple sensitization[1,11–13,16]: $I_2 \rightarrow Br_2 \rightarrow I_2$ (J.F. Goddard 1840) $I_2 = Br_2$; $Cl_2 = Br_2$; $I_2 = Cl_2$; $I_2 \rightarrow Cl_2$ (F. Kratochwila, J. & J. Natterer, E. Waidele 1840/41) $I_2 \rightarrow Br_2 \rightarrow Cl_2$ (F. Kratochwila, J. & J. Natterer 1840/41)	$2Ag_{(s)} + I_{2(g)} \rightarrow 2AgI$ $2Ag_{(s)} + Cl_{2(g)} \rightarrow 2AgCl$ $2Ag_{(s)} + Br_{2(g)} \rightarrow 2AgBr$	Chemical acceleration of the Ag surface. The surface is covered with Ag halogenide crystals. Halogenide mixture provides higher light sensitivity and shortens exposure time. AgCl: white appearance AgI: yellow appearance AgBr: cream yellow appearance
Exposure of silver halides (AgX)	$10AgX + h\nu \rightarrow 2Ag_{5(s)} + 5\,X_{2(g)}$	Decomposition of silver halides by light and formation of silver clusters (latent image formation)
Development by Hg vapour at ~ 60 – 120 °C (L. Daguerre 1839) Development without Hg (H. Becquerel 1840)[1]	$11Ag_5 + 45Hg_{(g)} \rightarrow 5Ag_{11}Hg_9$ $3Ag_5 + 20Hg_{(g)} \rightarrow 5Ag_3Hg_4$	Silver react with hot mercury droplets and form stable amalgam. Latent image developed by a yellow and/or red light treatment.
Fixation by sodium thiosulfate (J. Herschel 1839)[1–3,13,16]	$2\,Na_2S_2O_3 + AgX \rightarrow Na_3[Ag_8S_2O_3)_2] + NaX$	Dissolution of unexposed residual silver halides.
Post cleaning with water		Removal of the residual fixing solution
Gilding or toning with a AuCl solution[1–3,13,16]	$[Au(S_2O_3)_2]^{3-} + Ag \rightarrow Au + [Ag(S_2O_3)_2]^{3-}$	Increasing contrast and brilliance of the image
Post cleaning with water		Removal of the residual gold chloride solution

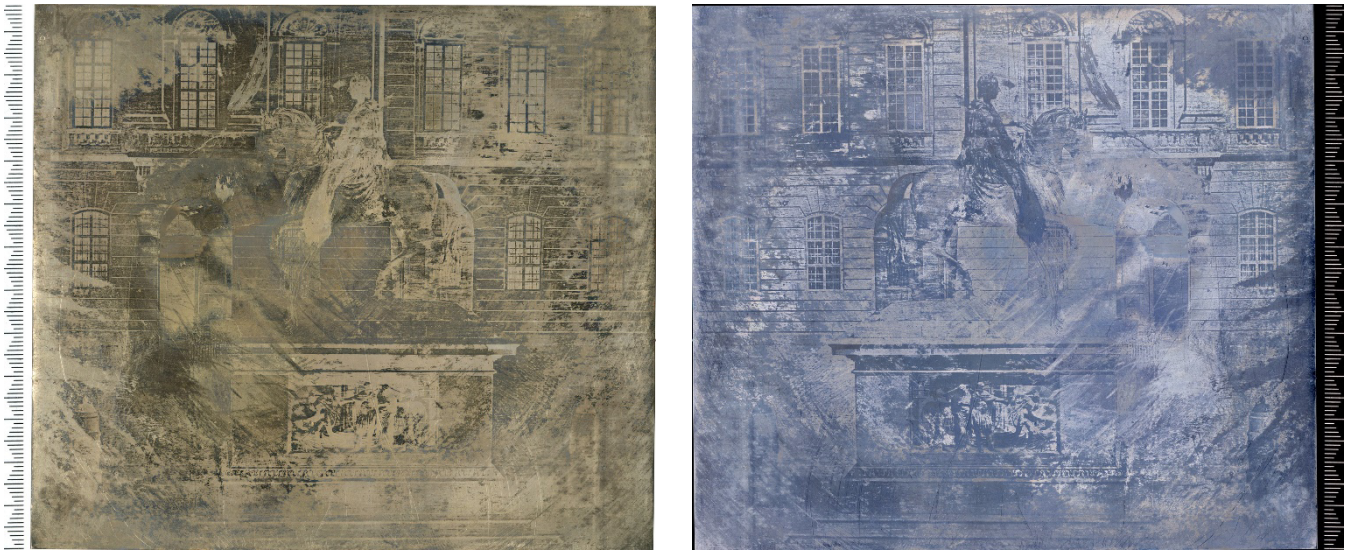

Figure 3. Joseph II's equestrian monument on Josefsplatz. Vienna. Etched Daguerreotype, Inv.Nr.: 83939/18, © Technisches Museum Wien, Austria. Plate size: 127 x 144 x 1 mm. **Left**: photograph. **Right**: inverted and horizontally mirrored photograph.

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The Austrian anatomy professor Joseph von Berres was interested in the generation of micrographs as a tool for microscopic research[13,17]. He recognized the potential of the newly discovered daguerreotype technique[20–23]. Since a daguerreotype is a unique object, Berres saw the need for the development of a reproduction technique. Already in 1840[3], he succeeded in producing printing plates for the first reproduction of photographs by etching daguerreotype plates. This etching technique is still widely unexplored, because no original etched daguerreotype plates have been discovered by now.

The knowledge of the physico-chemical processes associated with the above mentioned new photographic techniques is rudimentary up to date. The present study of the fundamentals of the above-mentioned novel procedures could be based on investigations of an etched daguerreotype plate probably photographed by the brothers Natterer and etched by Berres. It was recently discovered in the collection of the Technische Museum Wien [24]. This carrier plate is a silver-plated copper sheet typical for daguerreotypes and shows Joseph II's equestrian monument on Josefsplatz in Vienna (Fig. 3 left). Joseph II, the eldest son of the Austrian ruler Maria Theresa, was a Holy Roman Emperor and took over the Habsburg lands from his mother in 1780.

Results and Discussion

Surface Characterization

Surface characterization investigations were conducted in order to elucidate the manufacturing processes of daguerreotypes in Vienna of the early 1840s. The plate of the Joseph II's equestrian monument on Josefsplatz in Vienna retained its metallic brilliance (Fig. 3 left). The excellent depth of field and image quality despite the existing etched surface regions and various signs of aging can be best recognized by an inverted and horizontally mirrored photograph of the plate which represents the actual aspect on Josefsplatz. There, the camera was set up south of the monument at a window of Augustinertrakt, a side wing of the Hofburg, the former principal imperial palace (Fig. 3 right).

Optical micrographs and surface profilometry (Fig. 4) show that the daguerreotype plate represents an etched daguerreotype plate most probably designated for printing reproduction. Various profile levels - and even a flaw due to possibly an etchant splash - suggest this conclusion. The etched depressions are comparatively flat with a maximum depth of up to 6 µm.

A scanning secondary electron micrograph of the plate is shown in Fig. 5. In an EDX analysis, the primary electron beam interacts with the sample by repeated random scattering leading to a teardrop-shaped volume extending from less than 100 nm to approximately 5 µm into the near-surface region. The depth of this interaction volume depends on the electron's landing energy, the atomic number of the specimen and the specimen's density. The depth of the x-ray (EDX) activation, h can be appreciated by the following equation[25]

$$h = 0.0276\ m_a\ V^{1.67} / z^{0.89}\ \rho\ [\mu m] \qquad (1)$$

where m_a = atomic weight (g/mole), ρ = density (g/cm^3), z = atomic number, and V = electron acceleration voltage (kV). With a V of 20 kV and the respective values of Ag this relationship results in an EDX activation depth of ca. 1.4 µm. The silver coating on the copper substrate plate showed an average thickness of 7.3 ± 1.1 µm determined by an array of 36 x-ray fluorescence measurements spots. That shows that solely the Ag coating with an average thickness of 7.3 ± 1.1 µm has been analysed by EDX. A case

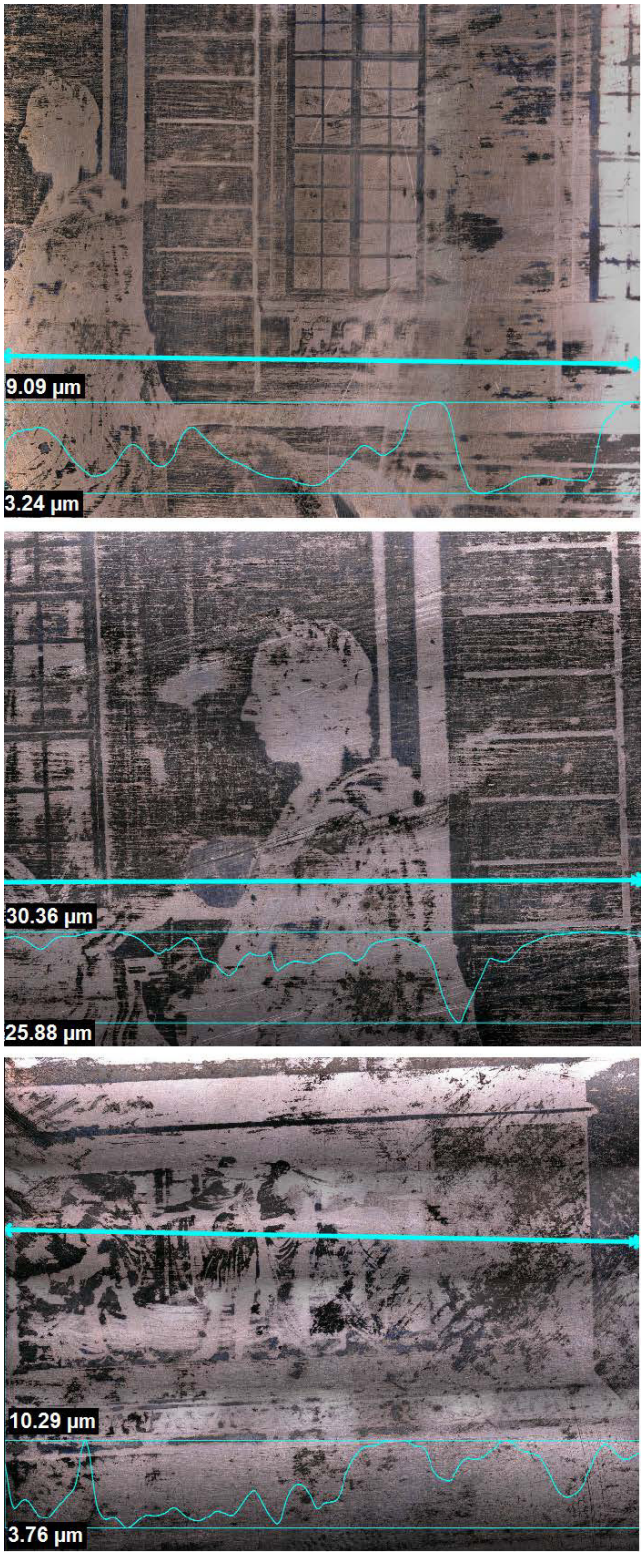

Figure 4. Optical micrographs with profilometry of the etched daguerreotype (Fig. 3). Three profile lines. Horizontal image edge: 513 mm (upper), 387 mm (middle), 272 mm (bottom).

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with finite Cu signals would suggest pores and/or inhomogeneities (e.g. due to etching) in the Ag layer.

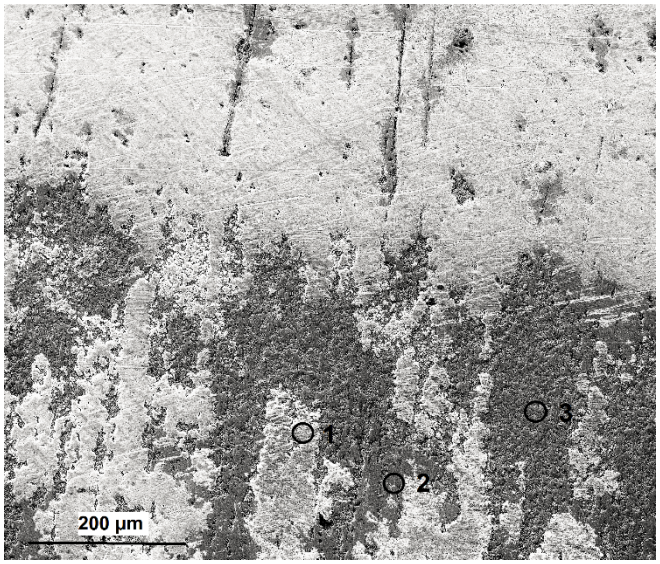

Figure 5. Scanning secondary electron micrograph of the etched daguerreotype (Fig. 3). Detail of the hoof front of the horse's right hindquarter. Three SEM/EDX measurement point are indicated.

Three SEM/EDX measurement points were chosen in the area of the hoof front of the horse's right hindquarter (Fig. 5). Three distinct morphological regions could be identified. Region 1 shows the highest secondary electron signal in contrast to region 2 and 3. This may suggest that the work function of this surface is lower than that of region 3, or/and that its lower conductivity leads to electron charging. A work function difference can be due to a different chemical composition of area 1 at variance to 2 and 3. The morphology of region 3 is typical for an etched surface which corresponds to low light exposure in contrast to the high exposure area 1 which does not exhibit etching features.

Table 2. EDX results (at%) of the regions 1-3 indicated in Fig. 5. Heliogravure on etched Daguerreotype.

	Region 1	Region 2	Region 3
S	14.39	0	0
Cl	1.10	0	0
Cu	1.35	1.27	3.63
O	4.37	8.05	20.86
Ag	38.72	52.74	37.56
C	38.97	37.26	37.37
Si	0.57	0.68	0.57
P	0.53	0	0

Region 1 represents a well light-exposed area where the photographic process based on silver halogenides led to the photon-catalysed reduction to colloidal silver nanoparticles (AgNPs). This photoproduct can be clearly seen in Fig. 6 left. The observed particle size distribution is between 30 nm and 120 nm, which is less than in characteristic daguerreotype highlight image microstructures between 100 nm and 2.5 µm[1,5]. Particularly the top AgNPs appear light and blurred indicating electronic charging possibly due to core-shell NP morphologies with insulating shell compositions. Such chemical conversions of the Ag core can be recognized by the EDX analysis resulting in a significant sulphur and a moderate chlorine signal besides oxygen (Fig. 6 right, Table 2). This finding suggests that the colloidal particles exhibited a conversion shell layer consisting of Ag_2O, Ag_2S, and some AgCl with low conductivity.

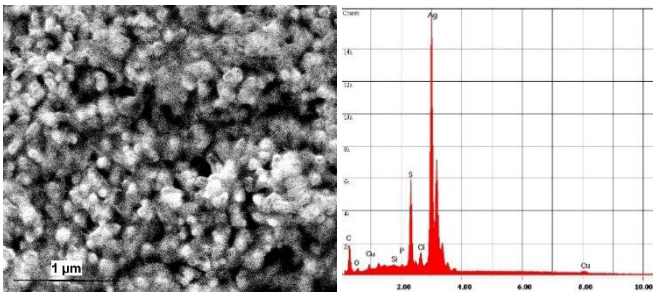

Figure 6. Scanning secondary electron micrograph (left) and EDX spectrum (right) of the etched daguerreotype (Fig. 3). Measurement point 1 in the white highlight.

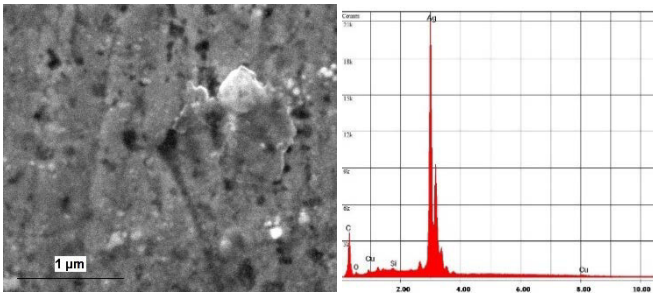

Figure 7. Scanning secondary electron micrograph (left) and EDX spectrum (right) of the etched daguerreotype (Fig. 3). Measurement point 2 in the midtone area.

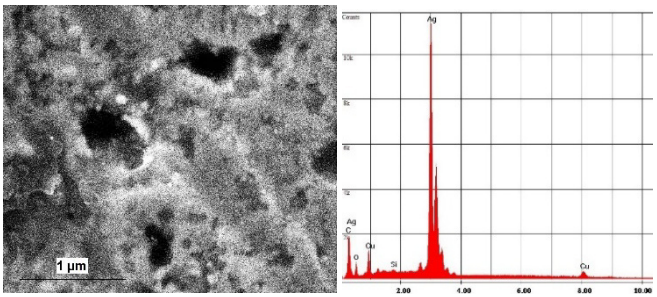

Figure 8. Scanning secondary electron micrograph (left) and EDX spectrum (right) of the etched daguerreotype (Fig. 3). Measurement point 3 in the shadow area.

These AgNPs and their conversion shells are practically absent in the midtone (Region 2) and dark tone (Region 3) areas (Fig. 5). The midtone region shows only some scratches from the original polishing treatment and some etching bits with diameters of < 100 nm (Fig. 7 left). The dark tone areas, in contrast, are dominated by larger etching bits with diameters of 200 – 400 nm (Fig. 8 left).

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Original polishing scratches are still observable despite extensive etching, however widened. The EDX analysis showed that any conversion layers involving Cl or S are absent (Fig. 7 right, 8 right, Table 2). The increased oxygen signal of the most extensively etched surface (Region 3, Fig. 8 right, Table 2) indicates a more abundant Ag_2O layer. The etching process exposed some copper substrate which is indicated by a somewhat higher Cu signal.

Photographic Procedure reconstruction

Silver Coating of the Copper Plate

Solid silver plates were rarely used [12]. In the beginning 1840ies galvanic silver plating was employed[1] and were available at relatively high costs in Vienna. Therefore, Kratochvila, J. and J. Natterer chose also electroless plating[26,27]. AgCl was dissolved in a NaCl solution[28]. Solid AgCl can form a chloroanion in the presence of highly concentrated Cl^- [29,30]

$$AgCl + Cl^- \rightarrow [AgCl_2]^- \quad (2)$$

The electroless reaction was the cementation of Ag from the dichloro silver anion on the copper plate. This is thermodynamically driven by the oxidative power of the silver electrode[31]:

$$Ag \rightleftharpoons Ag^+ + e^- \quad (U_0 = +0.80\ V) \quad (3)$$

with a standard potential U_0 which is much more positive than that of the Cu dissolution reactions

$$Cu \rightleftharpoons Cu_2^+ + 2\ e^- \quad (U_0 = +0.34\ V) \quad (4)$$

$$Cu \rightleftharpoons Cu^+ + e^- \quad (U_0 = +0.52\ V) \quad (5)$$

The overall electroless silver plating reaction (a cementation reaction) is therefore

$$[AgCl_2]^- + Cu \rightarrow Cu^+ + 2\ Cl^- + Ag \quad (6)$$

or

$$2\ [AgCl_2]^- + Cu \rightarrow Cu_2^+ + 4\ Cl^- + 2\ Ag \quad (7)$$

Sensitization

The first sensitization process based on the Daguerre's experience was the fumigation of the polished silver surface with iodine vapour[1–3,13] in a special fuming box (Fig. 2 left). There, photosensitive AgI was generated by the oxidation of the Ag substrate[5] (Table 1). However, iodine does not exhibit a sufficiently positive electrochemical potential for this reaction. An indirect route via the oxidant iodate can be suggested. It is well established that aqueous iodine chemistry is mainly governed by three reactions[10,32], namely the disproportionation of iodine to hypoiodous acid HIO, or hypoiodide IO^- anions (oxidation state +I), and to iodide,

$$I_2 + H_2O \rightarrow I^- + IO^- + 2\ H^+. \quad (8)$$

Hypoiodide is not stable and disproportionates to iodate (oxidation state +V) and iodide,

$$3\ IO^- \rightarrow 2\ I^- + IO_3^- \quad (9)$$

The overall reaction is

$$3\ I_2 + 3\ H_2O \rightarrow 2\ I^- + IO_3^- + 6\ H^+ \quad (10)$$

The oxidative power of the IO_3^- ion is sufficient at all applied pHs (mostly near neutrality)[33,34] to oxidize the Ag surface so that AgI can be formed as a photosensitive film:

$$6\ Ag + IO_3^- + 6\ H^+ \rightarrow 6\ AgI + 3\ H_2O \quad (11)$$

AgI exhibited a very low sensitivity[1,3].

A multiple sensitization by fumigation with bromine in addition to iodine was introduced practically in parallel by laboratories in England and Austria yielding an improved sensitivity[2,3,11,13]. Bromine, in contrast to iodine shows a sufficiently positive standard potential[31]:

$$Br_2 + 2\ e^- \rightleftharpoons 2\ Br^- \quad (U_0 = +1.0873\ V) \quad (12)$$

so that Ag (U_0 = +0.80 V) can be oxidized directly to the photosensitive phase AgBr.

The Viennese pioneers, F. Kratochwila, the brothers Natterer, and E. Waidele, extended the multiple sensitization procedures of photographic plates with chlorine gas[11–13,15]. They employed Cl_2 and Br_2 or I_2 concurrently, or in a series, first I_2 followed by Cl_2, or first I_2 followed by Br_2 and finally Cl_2.

The iodized surface was exposed to Cl_2 gas produced by a chlorinated lime ("Chlorkalk"), a mixture of calcium hypochlorite, $Ca(OCl)_2$, $CaCl_2$ and a $Ca(OH)_2$ solution[11]. The reactant of this mixture is CaCl(OCl). It can react with an acid such as carbonic acid from the atmospheric CO_2 producing Cl_2:

$$CaCl(OCl) + CO_2 \rightarrow CaCO_3 + Cl_2. \quad (13)$$

Cl_2 easily can oxidize the Ag surface due to its very positive potential

$$Cl_2 + 2\ e^- \rightleftharpoons 2\ Cl^- \quad (U_0 = +1.36\ V) \quad (14)$$

resulting in an AgCl film.

Exposure

The Viennese authors thus employed a silver halogenide (AgX) mixture as photosensitive phase[11]. The absorption of a photon results in the formation of a latent image based on Ag4 clusters[35]. A photoreaction can be assumed as follows:

$$8\ AgX + 4\ h\nu \rightarrow 2\ Ag_4 + 4\ X_2 \quad (15)$$

The exposure time in a Voigtländer's Camera Obscura was only within 5 s to 6 s in cloudy weather, within 2 s on a bright day, and in direct sunlight in an "unmeasurable" time. This novel technology allowed the unblurred high quality imaging of moving motifs such as portraits and street scenes for the first time.

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Development

The common development procedure for daguerreotypes was the formation of Ag amalgam particles next to the latent image Ag clusters[1,36]. The heated Ag plate was treated by Hg vapour.

Edmont Becquerel reported a development procedure based on AgI without the use of mercury in 1840. This method is related to the famous "Becquerel effect"[37] where AgI was exposed resulting in a latent image. This was further developed by a yellow and/or red light treatment. However, this ground-breaking invention did not yet assert itself against the method of Daguerre employing mercury[1,3,13].

In the following year, in 1841, also the Viennese Natterer brothers developed a method without mercury[12]. This novel procedure represented a breakthrough photographic technique due to the high sensitivity of the employed halogenide mixture. In the case of the least sensitive layer of AgI, a development procedure was reported[15]. This development process can be reconstructed as follows (comp.[38,39]):

$$2\ S_2Cl_2 + 2\ H_2O \rightarrow SO_2 + 4\ HCl + 3/8\ S_8. \quad (16)$$

The resulting SO_2 vapour reacts at the surface in humid atmosphere to sulphurous acid:

$$SO_2 + H_2O \rightarrow H_2SO_3. \quad (17)$$

It is remarkable that the deposition of the developer substance, sulphurous acid, was applied before the exposure. The sulphurous acid obviously acted as a reductant for the Ag halide (AgX) leading to AgNPs around the latent image Ag nuclei:

$$2\ AgX + H_2SO_3 + H_2O \rightarrow 2\ Ag + 2\ HX + H_2SO_4 \quad (18)$$

The development process already took place in the camera [28].

The authors even used sulphur bromide instead of sulphur chloride,

$$2\ S_2Br_2 + 2\ H_2O \rightarrow SO_2 + 4\ HBr + 3/8\ S_8, \quad (19)$$

and claimed a superb sensitivity[19].

Fixation

Josef Natterer performed the fixation either by potassium cyanide, KCN, or by sodium thiosulphate[19], $Na_2S_2O_3$. The fixation consisted in the dissolution of remnant halides:

$$2\ Na_2S_2O_3 + AgX \rightarrow Na_3[Ag(S_2O_3)_2] + NaX \quad (20)$$

$$4\ KCN + 2\ AgX \rightarrow 2\ K[Ag(CN)_2] + 2\ KX \quad (21)$$

Etching

The Viennese Joseph Berres succeeded in developing an etching technique in 1840 enabling first reproductions of the newly invented photographs[20–22,40]. He observed that the exposed Hg/Ag areas showed a high resistance towards etching with nitric acid. The unexposed areas covered by unreacted AgX could be attacked by the acid. His treatment of the exposed plates consisted of two operations, (1) the permanent fixation of the image and (2) the etching. The special image fixation procedure is passed down as follows[21].

Berres's fixation deviated from Natterer's procedure in that it prepared the follow-up etching step. The treatment of the plates in HNO_3 led to some dissolution of Cu at the reverse side and Ag on the exposed front side:

$$3\ Cu + 2\ NO_3^- + 8\ H^+ \rightarrow 3\ Cu_2^+ + 4\ H_2O + 2\ NO \quad (22)$$

$$3\ Ag + NO_3^- + 6\ H^+ \rightarrow 3\ Ag^+ + 3\ H_2O + NO \quad (23)$$

Due to its corrosive and oxidative effect, nitric acid is often used in printing technology for etching and is the oldest known mordant.

After fixing the image, Berres continues with the etching process[21].

In this second operation step (the "etching" step), a gum arabic solution was applied on the fixed image surface. Gum arabic, a mixture of glycoproteins and polysaccharides mainly consisting of arabinose and galactose, showed different wetting on the exposed AgNP regions and the unexposed bulk Ag regions. Obviously, the wetting was drastically reduced on the unexposed polycrystalline Ag region so that the follow-up etching step preferentially attacked the substrate. The formed depressions could accept the printing ink in the follow-up reproduction step. On the other hand, the exposed AgNP regions were much more wetted and thus protected by a stable gum arabic film.

In his report on the new developements in daguerreotype[19], Berres pointed to an important detail in the preparation of daguerreotype plates destined for later etching. Although it has been claimed that any carefully applied cleaning method or any cleaning agent could achieve a pure plate and a satisfactory image, he points out that the challenge of the daguerreotype process lies in the cleaning of the plates. Two techniques by Kratochwila and the physicist Anton Martin (1812-1882) were rated by him as the most reliable ones. Kratochwila simplified and shortened the time-consuming cleaning process by cleaning the polished plate with a distilled turpentine oil and cotton, followed by polishing with a bale of deerskin. Martin cleaned the plates with ethyl alcohol, distilled water, and powdered sheep bones on a soft deerskin. According to Berres, Martin's images exhibit an unsurpassed clarity and sharpness, and are recommended for the production of heliographies destined for printing. The turpentine-treated plates often still had a mist that made the image less pure and, due to a fine resin coating, prevented deeper penetration of the etching process[19].

Berres improved his etching procedure[19]. Obviously, Berres experimented also with amalgamated images[19]. The etch process was repeated until a sufficient depth was reached and was finished by rinsing in distilled water. He was able to achieve hundreds of prints[19]. Berres further reproduced original etched photographs by a process in which an auxiliary intermediate film of Au was electroplated from $AuCl_3$, and numerous Cu replica could be generated by electrotyping. Thus, innumerable photographic reproductions were possible for the first time.

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Deterioration

Deterioration processes generally observed with common daguerreotypes which contain Hg are absent in the present case. The plate does not contain Hg due to a different fixation process. Moreover, due to the absence of cover glasses – as were used with daguerreotypes – no influence of glass corrosion exists. Since the plate was kept completely open and without any protection during the long period of about 180 years, other corrosion processes could be observed in the present study.

The front side of the plate appears yellow-brownish in the middle and blue-greyish at the blurry edges (Fig. 3 left). It is not known whether the plate was smudged during the manufacture and etching process, or at a later stage, due to inadequate storage and handling. Particularly the left edge of the plate and the pavement area were strongly blurred. In addition, scratches, finger smudges and other blurred areas are visible as fine, dark and grey lines and spots. Due to the numerous grey scales and blurred areas, it was very difficult to distinguish between the physical damages and the chemical alterations of the surface. This suggests that complex deterioration mechanisms took place[1,7].

Unevenness's are visible on the back of the plate (Fig. 9). In the recesses there are residues of a dark coating (probably asphalt).

Figure 9. Reverse side of the etched daguerreotype (Fig. 3).

Along the right front side (Fig. 3 left), approx. 15 mm from the edge, a dark stripe can be observed, which probably comes from the mechanical fixture.

Examples of mechanical damages, such as scratches and wiped areas, are presented in Fig.10. Such damages are most probably old and may date back to the time of image production. Several deteriorations exist which look like remnants of splashes. A representative example on the hoof front of the horse's left hindquarter (comp. Fig. 4 right) is depicted in Fig. 10. A SEM image of another splatter reveals the etched morphology within that area (Fig. 11). This may allow the conclusion that the splashes may have been created during or shortly after the production process unintendedly by an etching liquid such as HNO_3.

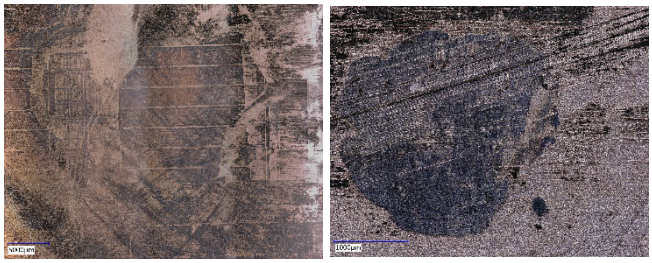

Figure 10. Optical micrographs of a spot-like deteriorated area of the etched daguerreotype (Fig. 3).

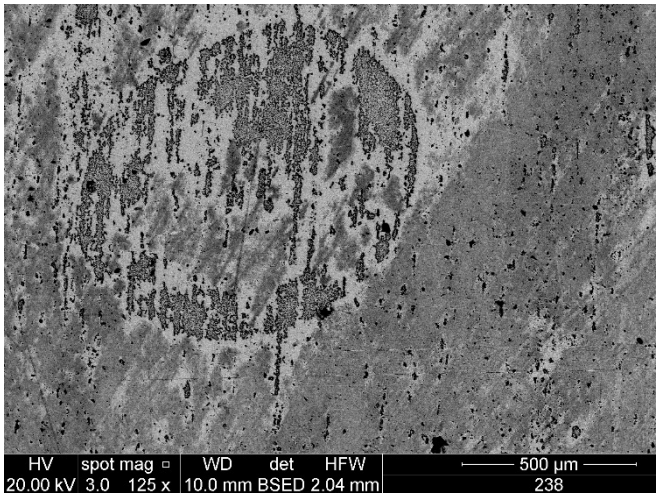

Figure 11. Scanning secondary electron micrograph of a spot-like deteriorated area of the etched daguerreotype (Fig. 3).

Summary

The physico-chemical fundamentals of the world-wide first photographic technology which allowed manifold reproduction has been evaluated (Table 3). This was performed by detailed investigations of a silver-plated copper plate daguerreotype, recently discovered in the collection of the Technisches Museum Wien. It depicts emperor Joseph II's equestrian monument on Josefsplatz in Vienna created most probably by the Viennese photographic pioneers, the brothers Natterer and Joseph Berres. Thus, the chemical processes involved could be identified.

The historically first sensitization process based on the Daguerre's experience was iodization. It resulted in a photosensitive film of AgI. The remarkable invention by the Viennese pioneers, F. Kratochwila, the brothers Natterer, and E. Waidele, consisted in the multiple sensitization of the photographic plates also with chlorine and bromine. On the investigated plate, however, only chlorine was detected. This suggests that in this case solely a chlorine gas treatment was applied so that Ag was oxidized to AgCl.

The common development procedure for daguerreotypes was the formation of Ag amalgam particles next to the latent image Ag clusters. Edmont Becquerel reported a development procedure based on AgI without the use of mercury in 1840, where AgI was converted to latent images (by the "Becquerel effect"). The development technique of the Viennese Natterer brothers in 1841

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could be reconstructed as the hydrolysis of S_2Cl_2 resulting in SO_2 and H_2SO_3, which acted as a reductant for the Ag halides, leading to AgNPs around the latent image Ag nuclei. The Natterer brothers also used S_2Br_2 instead of S_2Cl_2 and claimed a superb sensitivity. Josef Natterer performed the fixation of the developed image either by potassium cyanide, KCN, or by sodium thiosulphate, $Na_2S_2O_3$ that dissolved the remnant halides. This is supported by the finding that the surface analysis of the investigated plate revealed no Hg.

Table 3. Photographic procedure reconstruction.

Process	Reaction
Ag coating of the Cu plate	$2\ [AgCl_2]^- + Cu \rightarrow Cu_2^+ + 4\ Cl^- + 2\ Ag$
Sensitization	$2\ Ag + X_2 \rightarrow 2\ AgX$
Exposure	$8\ AgX + 4\ h\nu \rightarrow 2\ Ag_4 + 4\ X_2$
Development	$2\ AgX + H_2SO_3 + H_2O \rightarrow 2\ Ag + 2\ HX + H_2SO_4$
Fixation	$2\ Na_2S_2O_3 + AgX \rightarrow Na_3[Ag(S_2O_3)_2] + NaX$ $4\ KCN + 2\ AgX \rightarrow 2\ K[Ag(CN)_2] + 2\ KX$
Etching	$3\ Ag + NO_3^- + 6\ H^+ \rightarrow 3\ Ag^+ + 3\ H_2O + NO$

In the light-exposed area of the plate, a photon-catalysed reduction led to colloidal silver nanoparticles (AgNPs) with a size distribution between 30 nm and 120 nm. This is definitely less than Ag amalgam particle sizes typical for highlight image microstructures of daguerreotypes, which are between 100 nm and 2.5 µm. The colloidal particles exhibited a conversion shell layer consisting of Ag_2O, Ag_2S, and some AgCl.

The etched plate surface corresponds to low light exposure. In contrast, the high exposure area does not exhibit etching features. The AgNPs and their conversion shells are practically absent in the midtone and dark tone areas. These, in contrast, are dominated by larger etching bits with diameters of 200 – 400 nm. Any conversion layers involving Cl or S are absent while Ag_2O layers are abundant.

Joseph Berres succeeded in developing an etching technique in 1840 for the common daguerreotypes involving Ag amalgams. Thus enabled first reproductions of daguerreotypes. Original literature suggests that the exposed amalgam areas showed a high resistance towards etching with nitric acid. The unreacted AgX could be attacked by the acid. Berres applied a gum arabic solution on the fixed image surface before the etching step.

In the case of the investigated plate without Hg, one can assume that gum arabic was also applied. This treatment resulted in strong wetting of the exposed AgNP regions. The unexposed bulk Ag regions, on the other hand, showed negligible wetting so that preferential etching could take place there. The formed depressions allowed printing ink uptake in the follow-up reproduction step. Berres further reproduced original etched photographs by a process in which an auxiliary intermediate film of Au was electroplated from $AuCl_3$. Thus, innumerable photographic copper replica could be generated by electrotyping for the first time.

Deterioration processes generally observed with common daguerreotypes which contain Hg are absent in the present case. Scratches, finger smudges and blurred areas visible as fine, dark and grey lines and spots are most probably old damages and may date back to the time of image production. Remnants of splashes may have been caused unintendedly during the etching process.

Conclusion

In 1841, the Viennese Natterer brothers, medical students working together with their colleague Erwin Waidele developed breakthrough photographic procedures providing a hitherto unachieved high sensitivity. These and the first calculated objectives designed by the mathematician Josef Petzval enabled the earliest known photographs of moving street scenes. Joseph Berres was the first to succeed in etching heliogravures for intaglio printing and thus allowed reproducible photographic illustration.

Detailed physico-chemical investigations of the unique silver-plated copper plate daguerreotype depicting emperor Joseph II's equestrian monument on Josefsplatz in Vienna - recently discovered in the collection of the Technisches Museum Wien together with original reports of the involved pioneers – led to the elucidation of the world-first high-sensitivity photographic and reproduction processes.

These findings may serve for the future technological elucidation of early photographs from the first half of the 19th century. Moreover, this will support the recognition and verification of prints manufactured by etched daguerreotypes.

Experimental Section

A systematic materials analysis of the daguerreotype plate showing the Joseph II's equestrian monument on Josefsplatz in Vienna (Fig. 3 left) has been undertaken. An average Ag-layer thickness was evaluated by x-ray fluorescence (XRF; Roentgenanalytik Systeme GmbH & Co. KG, maXXi 5/PIN). Optical micrographs of the surface topography were recorded with a digital microscope (Keyence, VHX-5000) together with the z-scan techniques. Scanning electron microscopy (SEM) was combined with energy-dispersive X-ray spectroscopy (EDX; QUANTA FEG 250, FEI). The topography was imaged with secondary electron signals. Since secondary electrons are emitted from very close to the specimen surface very high-resolution images could be achieved. The composition was analysed with energy-dispersive X-ray spectroscopy (EDX).

Competing interests

The authors declare that they have no competing interests.

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Keywords: daguerreotypes, heritage science, photochemistry, photography, nanoparticles.

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Physicochemical characterization of electrodeposited printing plates from the early 1840s in Vienna

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ABSTRACT

The technology of electrotyping was successfully applied for the reproduction of printing plates shortly after its invention in 1838. In Austria, high-quality printing plates have already been produced at the beginning of the 1840s in the first laboratory for electrotyping in Vienna. However, little is known about the properties of electrodeposited printing plates from this early period. In this study the manufacturing process, surface structure, chemical composition, and corrosion properties of three electrotype plates from the Viennese laboratory were investigated. Two samples were intaglio plates made for printing and one was a relief negative for electrotyping reproduction. They exhibited no metal coating, whereas the third sample, a relief plate, was coated with silver to ease the separation from an electrotype copy. Thin colophony films with traces of vegetable wax were identified by ATR–FTIR spectroscopy and GC–MS. Multispectral imaging analysis by UV reflectance indicated a strong inhomogeneous distribution between elevations and depressions of the relief plate.

1. Introduction

Electrochemical metal deposition can be applied as electroplating or electrotyping (galvanoplasty, electroforming) [1]. The latter is an electrochemical method for forming metal parts that exactly reproduce a model [2–6]. The inventor of this process was the German physicist Moritz Hermann von Jacobi who reported his invention in St. Petersburg in 1838 [7] and published his experiments in a brochure entitled "Galvanoplastik" in 1840 [8].

Electrotyping was adopted for the reproduction of intaglio images from the beginning as a novel reproduction technology for graphic arts where copper reproductions of engraved metal plates were generated [9–15]. Until then, only a limited number of prints from the original engraving plate could be realized. Particularly in intaglio printing, the lifespan of the plate was limited because the quality decreased by mechanical wear. The invention of electrotyping served to overcome this limitation. Electrotyping allowed to produce any number of electrotype duplicates from the original engraving plate, and therefore an unlimited number of prints [10]. The impact of this new technology on the dissemination of art was compared with the invention of printing in 15th century, and its potential of spreading knowledge [9,11,16]. In 19th century, graphic art became increasingly popular ("graphics boom"). This boosted the development of new reproduction techniques as e.g. electrotyping. The value of limiting the size of an edition and of including the volume of the edition in the print number (e.g., "35/90" for the 35th print in a total edition of 90) was recognized not until ca. 1880. It became common that artists signed their print in pencil and numbered it to show the uniqueness of that print and the total edition size [16].

In electrotyping, a galvanic positive copy ("Basrelief, Matrize") [17] was generated from the original engraving which again was used as master relief for a further electrodeposition step leading to the final printing plate ("Matrize") [17]. The original copper engraving ("Urtypus") was not used for printing production and therefore, suffered no mechanical wear. Moreover, the final printing plate ("Matrize") was more hard-wearing than the original because it exhibited a much denser metallurgical structure than the engraving ("Urtypus") which was based on a rolled copper sheet. This could theoretically extend the number of prints indefinitely.

A diluted sulfuric acid (H_2SO_4) solution saturated with copper sulphate ($CuSO_4$) served as electrolyte [6,13,17–19]. Sometimes zinc sulphate ($ZnSO_4$) was added to this solution in order to reduce the brittleness of the deposited copper [13]. The original engraving ("Urtypus") as well as the galvanic positive copy ("Basrelief, Matrize") were cleaned before they were introduced into the galvanic bath. A

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reported version was a treatment with turpentine and ethyl alcohol followed by diluted nitric acid (HNO_3) [13]. Another report describes the cleaning by a caustic potash (KOH) solution and a treatment with greases or oils, such as olive oil, which was mechanically reduced by paper wiping and brushing [17,20]. This was the prerequisite for the separation of the copy from the master plate. An alternative to this grease and oil overlay was the electroless or galvanic silver deposition based on a cementation reaction between the copper substrate and a AgCl/NaCl solution [13]. The losses of copper metal were so low that no quality change was observed.

Shortly after the invention of electrotyping it was rapidly developed to an unrivalled quality at the first Austrian laboratory for electrotyping established and run by Franz Theyer and Erwin Waidele in Vienna from 1841 on [9,11,29–32,21–28]. More than 70 partly silver or gold-plated copper electrotyped artefacts were rediscovered in the collection of the Technisches Museum Wien, Austria [31]. They provide an important information on the structure of depressions in various intaglio-printing techniques. However, the knowledge concerning the production of early electrotype artefacts for graphic arts is still very restricted. Solely general information can be found in early publications and technical encyclopaedia from the 19th century [3,4,15]. Since then, no scientific research of the used materials and techniques has been undertaken.

In the present study, investigations of the surface film nature and morphology of three electrotype plates manufactured in 1844 in Austria were performed. Conclusions were drawn in respect to the manufacturing and deterioration processes, as well as possible conservation treatments.

2. Material and methods

The three electrotype plates (Figs. 1 and 2) of interest were manufactured in 1844 by the first commercial laboratory for electrotyping in Austria, established and run by Franz Theyer in the period 1839–1851 [9,11,29–31,21–28]. From Theyer's collection, one silver covered electrotype plate "Hl. Joseph" (Technisches Museum Wien, Austria, Inv.Nr.: 84183/3) was chosen for a chemical surface investigation (Fig. 1c). The following text is engraved below the image: "St. Joseph, der du auf Erden den Herrn der Herrschenden Dir unterthänig gesehen hast, bitte für uns! Jos. Führich m.v. Leop. Beyer sculpt".

The analysis options were very limited due to the size of the objects (Table 1). No destructive methods were chosen [33–35]. Morphological investigations were performed by optical microscopy (z-scans; Keyence, VHX-5000). Scanning electron microscopy (SEM) and energy-

Fig. 1. Electrotype engraving copper plates (a–c) and print (d). "St. Joseph", 1843, Vienna. Technisches Museum Wien, 23 × 30 cm. (a) intaglio plate (Inv.Nr.: 84183/1), (b) intaglio plate (Inv.Nr.: 84183/2), (c) relief plate, (Inv.Nr.: 84183/3), (d) print from plate 2 (Inv.Nr.: BPA-015565-10).

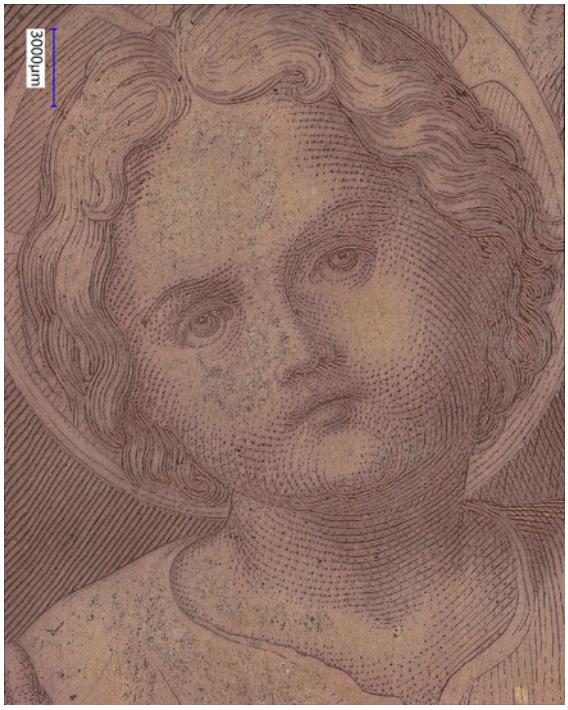

Fig. 2. Microscopy image (z-scan) of a detail of the electrotype engraving relief plate in Fig. 1c. "St. Joseph", 1843, Vienna. Technisches Museum Wien, 23 × 30 cm. plate (Inv.Nr.: 84183/3).

Table 1
Electrotype plates. "St. Joseph", 1844, Vienna. Technisches Museum Wien.

Description	Inv.Nr.	Historical labelling on the wrapping paper in the archive	Dimensions [mm]
Intaglio plate	84183/1	"St. Joseph, der du auf Erden den Herrn der Herrschenden Dir unterthänig gesehen hast, bitte für uns! Jos. Führich m.v. Leop. Beyer sculpt."	224 × 309 × 1
Intaglio plate	84183/2	"Druckplatte der hl. Josef - gestoch. v. Beyer. Mit der Aufschrift aus Theyers Laborat. 844 Den 27 April 40 Drucke Original"	224 × 309 × 1
Relief plate	84183/3	"Der hl. Joseph nach Führich gest. v. Beyer Reliefplatte"	225 × 298 × 2

dispersive x-ray fluorescence spectroscopy (EDX) were not accessible due to the size of the object.

Ultraviolet, visible and infrared reflection, but also visible fluorescence imaging investigations in the spectral range from 320 nm to 1550 nm were undertaken by a multi-spectral imaging system (MuSIS 2007, Art Innovation, Hengelo, The Netherlands) to identify the surface distribution of any organic coatings [36]. Six imaging modes could be employed: visible, infrared in three bands (– 700 nm to1550 nm), false-colour infrared, fluorescence, and ultraviolet (365 nm). The ultraviolet imaging mode provided a sensitive tool to detect organic thin films. A black light UV lamp (100 W, 365 nm, Hg I-line) was utilized as source. In the visible recording mode, two halogen tungsten lamps were placed at 45 degrees in respect to the sample surface. The plate was mounted on a black canvas background with the aim of reducing stray light scattering.

The quantification of silver film thickness of silver covered electrotype plate (Technisches Museum Wien, Austria, Inv.Nr.: 84183-3, Fig. 1c) by x-ray fluorescence spectrometry (XRF; Röntgenanalytik Messtechnik GmbH, maXXi 5 PIN) was not successful. Values were below the detection limit.

The chemical nature of surface films was analysed by means of gas chromatography coupled with mass spectroscopy (GC–MS) analysis and attenuated total reflectance FT-IR spectroscopy. The GC–MS analysis (Agilent Technologies, USA, 6890N gas chromatograph connected to a quadrupole mass spectrometer, model 5973N) of the resinous binding media was based on the esterification of resinous acids followed by the identification of particular resins according to their resinous acid methyl esters.

Infrared spectroscopy is a powerful tool in heritage science [37]. The attenuated total reflectance FT–IR spectroscopy (PerkinElmer, Spectrum Two FT-IR Spectrometer, designed for large specimen equipped with an ATR accessory, GaldiATR PIKE) was performed in the wavenumber range between – 400 to 4000 cm^{-1}. Eight scans and a spectral resolution of 4 cm^{-1} were chosen. The spectral processing was done by applying a baseline correction and a smoothing factor for noise reduction (PerkinElmer Spectrum software). FTIR signals were observed on multiple spots. Selected waxes, oils, and varnishes served as reference samples.

3. Results and discussion

These three electrotype plates (Fig. 1) show the high-quality standards of the Theyer's laboratory [9,11,38,39]. This can be particularly observed in a detail example (Fig. 2). The first two plates, Fig. 1a and b, exhibit a warm orange tone and high gloss. Rims, ~1 cm from the edges, appear filed and polished. The surfaces of all three plates show numerous scratches, which exhibit local corrosion products in contrast to the rest that preserved the bright colour and mirror-like gloss.

An optical microscopic profile evaluation allowed the identification of the first two plates as intaglio engravings (Fig. 1a and b), and the third silver–plated as an electrotyped relief [20] (Fig. 1c). The grooves of the intaglio plates (comp. Fig. 1a and b) exhibit depths up ca. 40 µm (Fig. 3a and b). The elevations of the electrotyped relief (comp. Fig. 1c) show heights of up to ca. 40 µm (Fig. 3c).

Multispectral imaging analysis provided convincing results by UV reflectance and VIS imaging (Fig. 4). A low UV reflectance indicates a strong absorption on high relief areas, whereas a high UV reflectance a low absorption on depression areas. That means that an organic film (see below) is distributed inhomogeneously on the sample. Obviously, the film application reached preferentially the high relief areas.

Horizontal scratches appear light indicating low UV absorption and thus a missing (removed) organic film. They are not observable in the VIS image demonstrating that they belong to a distinct layer different from the metal plate. These mechanical damages were probably introduced during the storage period.

The plates were analysed by ATR–FTIR in order to identify organic coatings. As reference served a copper plate covered with a native oxide layer exhibiting a characteristic Cu_2O (cuprous oxide) vibration around 620 cm^{-1} (Fig. 5, Table 2). This peak was considered as a reference for the coated originals. The carbonyl region (–1550 to 1800 cm^{-1}) and the fingerprint region (–500 to 1550 cm^{-1}) were evaluated. Resins, varnishes and vegetable wax coated on Cu plates served as IR reference samples (Table 2). The C═H vibration bands between 600 and 1450 cm^{-1} were compared with the data of various natural varnishes. The strong C═C bands at 1520–1540 cm^{-1} and 1610–1650 cm^{-1} of the intaglio and the relief plate could not be observed with the copal, dammar and linseed oil samples, butcorrelated with colophony. The absorption bands at 600–640 cm^{-1} in the fingerprint region due to C-H rocking vibrations indicate hydrocarbon waxes or colophony [37,40–42]. A C═O band around 1700 cm^{-1} are practically absent indicating low oxidation. Colophony ages by thermal, biological and photo degradation resulting in the aromatization of unsaturated cycles and hydroxylations [42]. This could be monitored by FTIR.

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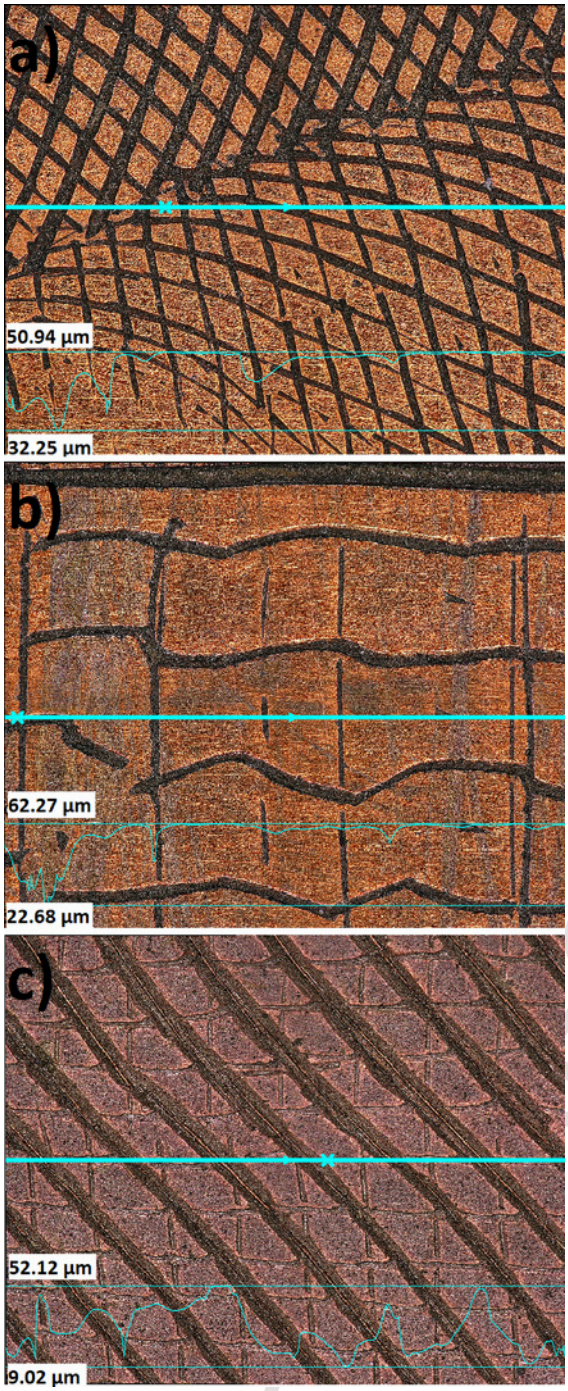

Fig. 3. Optical micrographs with profilometry showing typical profile lines. Electrotype engraving copper plates "St. Joseph", 1843, Vienna. Technisches Museum Wien. (a) intaglio plate (Inv.Nr.: 84183/1), (b) intaglio plate (Inv.Nr.: 84183/2), (c) relief plate (Inv.Nr.: 84183/3).

Wax and colophony can efficiently protect copper from corrosion [35,43,44]. Such a coating is practically irreversible applied to a cleaned metal and may have a long-term protective action in repetitive printing steps and in storage. Before the introduction of synthetic lacquers in the 1900s, colophony was commonly used alone or in mixtures with e.g. wax or linseed oil as surface protection for musical instruments, furniture, paintings and in arts and crafts [45]. Colophony was also often applied in certain manufacturing processes as a recess lacquer or cover lacquer. It has long been used extensively in lithography and, in general, for objects that have been partially etched. In the 19th and 20th centuries this covering method was also used in the production of patterned sheet metal, which was often provided with a fine decoration by the transfer printing process [46].

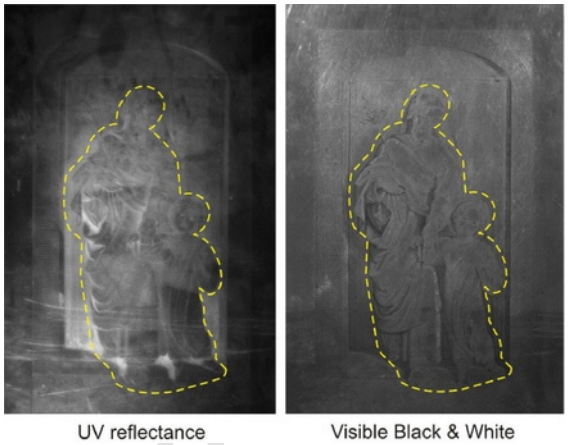

Fig. 4. Multispectral imaging analysis of the electrotype engraving intaglio plate "St. Joseph", 1843, Vienna. Technisches Museum Wien (Inv.Nr.: 84183/2). UV reflectance image and black and white photography.

A further analysis of the coating on the intaglio plate (Inv.Nr.: 84183/2) was performed by GC–MS [40]. The coating material was taken from the surface by a cotton swab wetted in a solvent mixture (EtOH:i-octane, 1:4). The extract was then evaporated, and the solid residues analysed. The sample is composed of a series of fatty acids and traces of pine resin such as colophony [42] (Fig. 6). This is in accordance with the ATR–FTIR results (Table 2). In comparison to the chromatogram of cotton swab blank sample, the intensities of fatty acids, namely palmitic acid and stearic acids (Pa, St) are higher, what could suggest that fatty acids are not only remnants from the cotton swab, but they are also from some additional fat impurities caused by the handling of the metal plate. The presence of an oil-resinous coating (dicarboxylic acids, Su, Az) in minute amounts overlapped with the signal of the fat impurities.

4. Conclusions

A physicochemical characterization of the manufacturing processes, the surface structure, the chemical composition, and the corrosion properties of three electrotype plates with the same motif of St. Joseph manufactured by the Laboratory of Franz Theyer and Erwin Waidele in Vienna, Austria, was performed. The surface micro-morphology revealed that two samples were intaglio made for printing and one represented a relief negative for electrotyping reproduction. The intaglio types showed no metal coating, whereas the relief plate was covered with silver to enable an easy separation from an electrotype copy. Thin organic films were identified on this intaglio as mainly colophony with traces of vegetable wax by ATR–FTIR spectroscopy and GC–MS. However, an exact assignment of the colophony wax coating and its significance on the electrochemically deposited printing plates could not be clearly made. It is quite conceivable that this coating played a role in the manufacturing process, but it also might be applied as surface protection.

The depths of the intaglio grooves and the elevations of the electrotyped relief (comp. Fig. 1c) were up to 40 µm. Multispectral imaging analysis by UV reflectance indicated a strong absorption on high relief areas. Obviously, an organic film was applied solely on the elevations not reaching the depressions. Scratches on all samples were probably introduced during the storage period.

With this study providing new information on the electrochemical reproduction of original printing plates, future identification of graphic prints and the elucidation of the 19th century's printing techniques may be facilitated.

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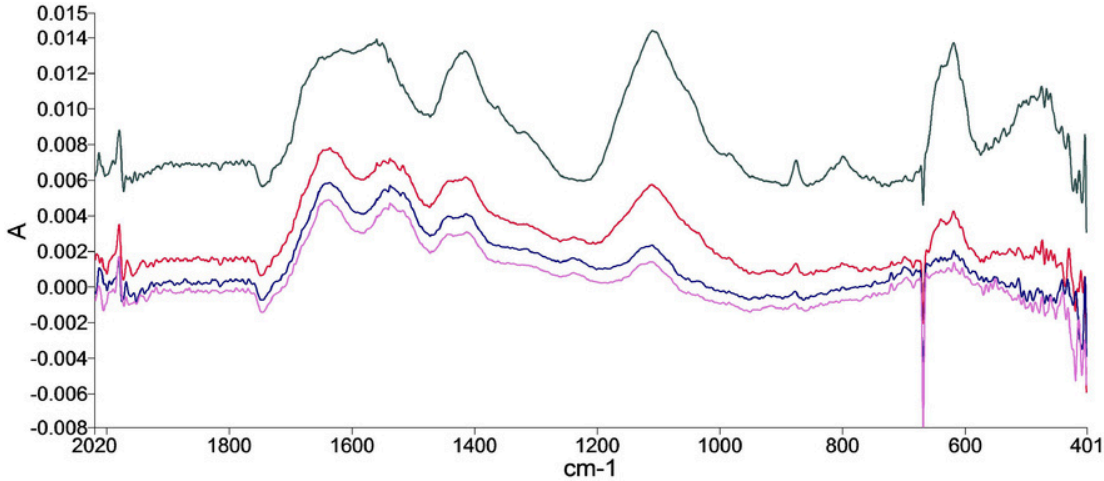

Fig. 5. ATR–FTIR spectra of the electrotype engraving relief plate "St. Joseph", 1843, Vienna. Technisches Museum Wien (Inv.Nr.: 84183/3).

Table 2
ATR–FTIR results of an intaglio plate (Inv.Nr.: 84183/2) and an electrotype engraving relief plate (Inv.Nr.: 84183/3). "St. Joseph", 1844, Vienna. Technisches Museum Wien. Fingerprint bands [cm^{-1}] in comparison with those of natural varnishes and vegetable wax.

Intaglio	Relief	Colophony [42]	Copal	Dammar	Linseed Oil	Wax	Bonds
640 (s)	600–640 (s)	652			680	635	CH_x
	800						
	880	910		880 (s)			
	980	980	970 (s)	980		950	
1120 (s)	1110 (s)	1107	1080	1100	1080	1070 (s)	
			1140 (s)	1160 (s)	1160 (s)		
1230	1230	1239	1220 (s)		1220	1250	
1400 (s)	1410 (s)	1365	1380 (s)	1380 (s)	1370	1360	
	1450 (s)	1450	1450 (s)	1440 (s)	1450(s)	1460	
1520 (s)	1540 (s)	1496					C═C
1640 (s)	1610–1650 (s)	1610–1615				1640 (s)	C═C stretch
		1697	1710 (s)	1700 (s)	1720 (s)	1730	C═O

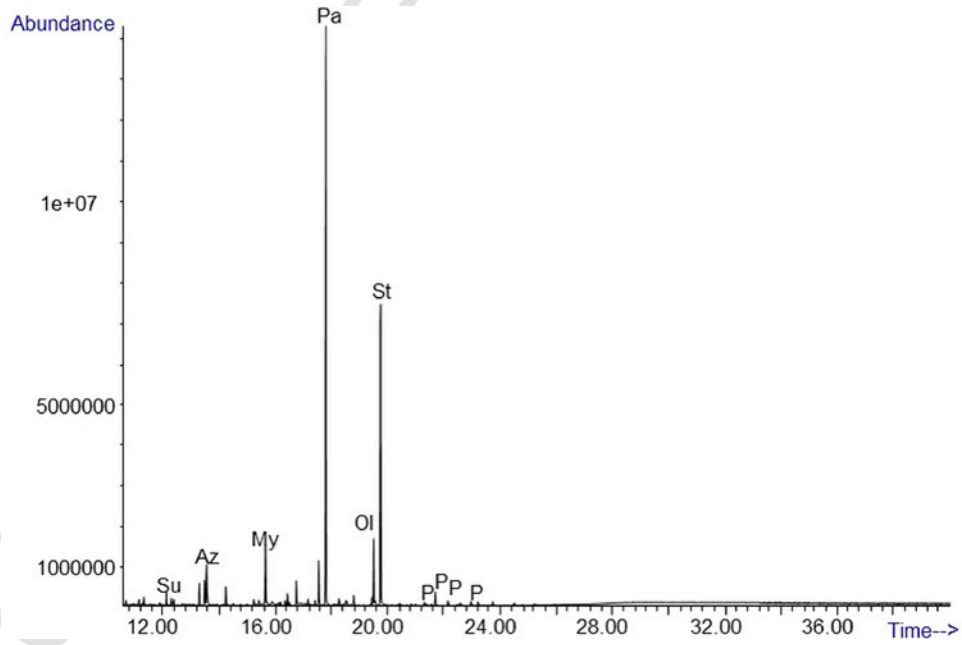

Fig. 6. Chromatogram (GC-MS) of the coating material on an electrotype intaglio plate. "St. Joseph", 1843, Vienna, Technisches Museum Wien (Inv.Nr.: 84183/2). Su: suberic acid. Az: azelaic acid. My: myristic acid. Pa: palmitic acid. Ol: oleic acid. St: stearic acid. P: diterpenes of pine resin (Pinus species).

Declaration of Competing Interest

None.

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