ICOM-CC València 2023
20th Triennial Conference

PHOTOGRAPHIC MATERIALS

Carl August Steinheil's pioneering daguerreotypes: Nondestructive investigation of his production and processing methods

Eva Mariasole Angelin
Conservation Science Department,
Deutsches Museum
Munich, Germany
e.angelin@deutsches-museum.de

Clarimma Sessa
Chair of Conservation-Restoration, Art Technology and Conservation Science,
Technical University of Munich
Munich, Germany
clarimma.sessa@tum.de

Martin Jürgens
Rijksmuseum
Amsterdam, The Netherlands
m.juergens@rijksmuseum.nl

Élia Roldão
Department of Conservation and Restoration,
NOVA School of Science and Technology
Caparica, Portugal
e.roldao@fct.unl.pt

Cornelia Kemp
Research Institute,
Deutsches Museum
Munich, Germany
c.kemp@deutsches-museum.de

Marisa Pamplona*
Conservation Science Department,
Deutsches Museum
Munich, Germany
m.pamplona@deutsches-museum.de

*Author for correspondence

Keywords

daguerreotype, photography, gilding, electroplating, technical history, nondestructive multi-technique approach

Abstract

This study highlights Carl August Steinheil's photographic processes and sheds light on the early history of daguerreotypes in Germany. The oldest surviving daguerreotypes by Steinheil (47 plates dated ca. 1839–1841) are conserved at the Deutsches Museum in Munich. The study integrates historical sources with analytical data collected from Steinheil's rare photographic objects to gain insight into his production and processing methods. These yet unstudied daguerreotypes were investigated using X-ray fluorescence, external reflection Fourier transform infrared spectroscopy, and ultraviolet fluorescence. Seven plates were compared to reconstructed daguerreotypes produced in the laboratory following historical

INTRODUCTION

On September 5, 1839, only shortly after the announcement of the daguerreotype process at the Academy of Sciences in Paris, two daguerreotypes were exhibited at the Kunstverein in Munich (*Allgemeine Zeitung* 1839). They had been taken by the physicist Carl August Steinheil (1801–1870), who was a member of the Bavarian Academy of Sciences and a university professor of mathematics and physics. From 1835 on, Steinheil was active in various fields of research, until, together with his sons Eduard and Adolph, he founded his own lens manufacturing company, Optische und astronomische Werkstätte C. A. Steinheil, in 1855.

Steinheil's many interests also included the study of the still nascent phenomenon of electrical currents. New batteries opened the door to many processes, including electrolytic metal deposition, practiced as galvanizing (electroplating) and galvanoplasty (electrotyping), the latter having been discovered by Moritz Hermann von Jacobi (1801–1874) (Jacobi 1840).

Contemporary sources recount Steinheil's experiments of electroplating with gold and copper to safeguard the daguerreotype images by making them physically more durable, thereby avoiding the use of a glass sheet for their protection (*Allgemeine Zeitung* 1840, *Gelehrten Anzeigen* 1842), and changing their hue (Alexander 1840, 298–299). Both methods were an alternative to the chemical gilding introduced by Hippolyte Fizeau (1819–1896) in 1840 (Fizeau 1840), which soon became the standard process for gilding daguerreotypes.

What distinguishes the beginnings of photography in Munich are the unusually rich holdings of surviving photographs, related materials, and written sources. As early as 1837, Franz von Kobell (1803–1882) had experimented with paper photography, of which 30 photographs are preserved at the Deutsches Museum. Steinheil's daguerreotypes in the same collection are supplemented by a wealth of notes from his estate, minutes of meetings at the Bavarian Academy of Sciences, and digitally accessible press releases. These documents from the beginnings of photography in Germany formed the basis for examining Steinheil's daguerreotypes in preparation for a comprehensive publication by Dr. Cornelia Kemp that will be published in 2023.[1] It became apparent, however, that there is a lack of detailed, original information on Steinheil's electrolytic techniques and materials, and the diversity of his experiments makes it complex today to understand

practice. A principal component analysis model demonstrated that significant differences between ratios of copper, silver, and gold were present. XRF analysis revealed that the differentiation between chemical and electrolytic gilding is not straightforward. Shellac and diterpenoid resin were identified, and the possibility of copper electroplated daguerreotypes is discussed.

how he worked. For this reason, visual examination and nondestructive scientific analysis of a selection of plates was carried out to supplement historical research with material-based evidence. This study concentrated on Steinheil's electrolytic gilding and copper plating methods.

CASE STUDIES

Of the 47 plates, eight have a strong golden appearance, seven have a matte surface with a barely visible image that appears to have a slight relief, ten have unusual colors, and the rest are bare plates. In the whole collection, only three plates are framed with a protective glass cover and have well-preserved images. The collection is partially preserved in cardboard boxes and original wooden boxes.

The subjects of the photographs include city views, self-portraits, and reproductions of other printed images. Correspondence from 1942 between Dr. Rudolf Loher (1900–1975) (occupational physician at Steinheil's company and a private collector of photography) and Prof. Erich Stenger (1878–1957) (Head of the Institute of Applied Photochemistry, Technical University, Berlin) mentions that several plates were in poor condition. Consequently, some daguerreotypes were treated by Prof. Stenger with a cyanide solution in order to recover the visibility of the tarnished images (Deutsches Museum Archive 1942). However, no information on the precise treatment was found.

For this study, seven daguerreotypes that appear to be representative of Steinheil's work on various gilding methods and copper electroplating were selected. Four were well-preserved with yellowish images (T1, T3, T5, T6), two had a more neutral hue (T28, T29), and one appeared to be experimental (T26). Two of these were golden in color on both front and back (T5 and T6). Five plates were circa 5 × 7 cm in size (T1, T3, T5, T6, T26) and two were squarish, at circa 7 × 8 cm, with round images (T28, T29) (Figure 1).

Figure 1. Overview of the seven daguerreotypes selected for this study. Each is labelled with a part number within the overall inventory number of "1965"

ANALYTICAL METHODS

Microscopic and ultraviolet (UV) fluorescence photographs were taken of both sides of the plates. UV-A and UV-C images were particularly useful in revealing the presence of organic substances, which were subsequently identified by external reflection Fourier transform infrared spectroscopy (ER–FTIR). The elemental composition of the daguerreotypes was investigated by X-ray fluorescence (XRF) on individual spots (1 mm^2) and scanned areas (10×10 mm^2) on the front and back of the plates. XRF spectra were used as source data for the creation of principal component analysis (PCA) models. Details are given in the Appendix.

MODERN RECONSTRUCTIONS

Steinheil's processes were reconstructed to create samples with a known treatment that were used as references for visual identification and for instrumental analysis. At the Rijksmuseum (Amsterdam), two daguerreotypes were made on silver roll-clad copper plates that were sensitized with iodine and bromine, exposed in a camera, developed over hot mercury fumes, and fixed with sodium thiosulfate solution. After washing and drying, one plate (M11) was given thinly deposited electrolytic copper coatings of increasing thickness. The second plate (M14) was gilded with Fizeau's chemical method.

RESULTS AND DISCUSSION

XRF detected copper (Cu), silver (Ag), and mercury (Hg) on all of the analyzed daguerreotypes that had a clearly perceptible image, indicating that these were silvered copper plates that were developed with mercury vapors, following Daguerre's original recipe.

Steinheil was aware of the use of halogen mixtures to improve the light sensitivity of the plates.[2] However, neither bromine (Br) nor iodine (I) were identified by XRF. Even though low signals of chlorine (Cl) were detected, it was not possible to conclude which halides Steinheil used to sensitize the plates, as either they were removed during fixing or fell below the XRF detection limit. Steinheil was able to photograph himself with open eyes without motion blurring and with extraordinary clarity and detail (Figure 1, plate T28), indicating a short exposure time. This could support the hypothesis of him having used a halogen mixture instead of only one halogen to sensitize the plate.

Elemental components of the original plates

A PCA model using the XRF spectra collected on the front of the daguerreotypes was created (Figure 2). Based on the interpretation of the loadings, PC1 mainly considered the variance between the silver and copper signals, whereas PC3 considered all peaks, including the gold (Au) line, which could be associated with a gilding process. In the score plot, PC1 discriminated between two main groups, namely the T1 and T3 (higher silver signal) and the T5, T6, T28, and T29 plates (higher copper signal). The differences in relative signal intensity of Ag and Cu may have resulted from the different thicknesses of the metal layers, which result from the production methods (roll-clad plates versus electroplated plates, or even electroplated roll-clad plates), and/or repeated polishing of the silver layer by Steinheil himself. Plates T28 and T29 had a "30" hallmark, which indicated that the plates were made of one part silver and

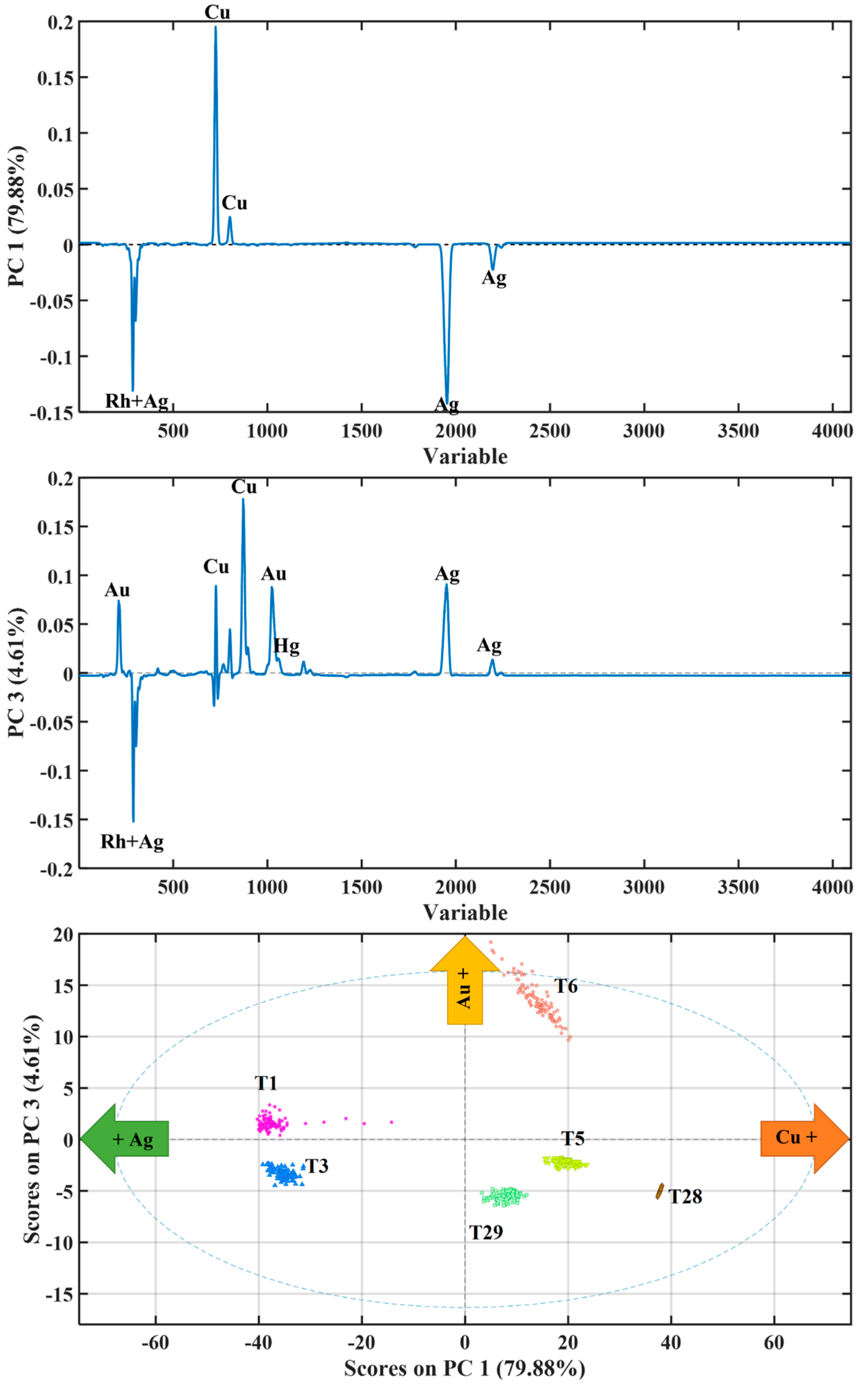

Figure 2. (Top) Loading plot of PC1; (middle) loading plot of PC3; (bottom) score plot of PC1 versus PC3 for a model composed of ten XRF spectra recorded on the front of daguerreotypes T1, T3, T5, T6, T28, and T29

29 parts copper (Lerebours 1843, 29). The plates also had, respectively, an embossed four- and six-pointed star at their bottom corners, suggesting French provenance (Cartier-Bresson 1989).

Chemical and electrolytic gilding

Au was detected in different amounts and locations on all of the daguerreotypes. Plates T1, T3, T5, and T6 were shown to have Au on both sides of the plate, whereas T28 and T29 only had it on the front (Figure 3). Of particularly interest was the higher Au signal detected on T6, which differentiated it as an independent cluster in the PCA model (Figure 2) and made it unique within this group of daguerreotypes.

Steinheil is reported to have electrolytically gilded (gold-plated) daguerreotypes in 1842.[3] In a typical electrolytic (galvanic) setup, two metal plates are placed into an electrolyte, a solution containing metal ions. The metal to be plated is the cathode and the opposite plate, the anode, supplies the solution with ions. The closed electrical circuit of a battery enables the transport of the ions from the anode to the cathode, on which a distinct metal layer is formed as deposition progresses. Timbs et al. (1842, 146) and Elkington & Co. (1844, 17–19) describe the use of a cyanide-bath as an electrolyte for the electrodeposition of Au.

Chemically gilded daguerreotypes typically display Au only on the front, since the gilding solution is poured onto the horizontal plate. In the electrolytic setup, however, the daguerreotype is immersed in the electrolyte, so gold deposits on both sides of the plate unless a protective organic coating such as wax or a varnish has previously been applied to the back. Following this rationale, the presence of Au only on the front of T28 and T29 suggests that they were gilded either with Fizeau's chemical method or electrolytically but then with a protective back coating, which however was not detectable under UV-fluorescence examination. The plates T1, T3, T5, and T6 had Au on both sides, so they were probably gilded electrolytically. Interestingly, daguerreotype T6 not only contained the most Au, but it also had, at its upper right corner, a small area in which no Au was present on either the front or the back (Figure 4). The lack of Au at this location deserves further investigation, especially in terms of the technical aspects of galvanic gilding or other post-processing methods.

The variable signal intensity of Au detected on these daguerreotypes could relate to different conditions in the electrolytic process, such as current intensity, electrodeposition duration, and solution concentration, but the extent of chemical gilding is also influenced by temperature, duration, and the makeup of the solutions. The Au signal of the chemically gilded reconstructed plate (M14) was found to be lower than that of Steinheil's plates (Figure 3). These findings indicate that the determination of the Au content via XRF cannot be used as a sole method to discriminate between electrolytic and chemical gilding, at least not without creating further reconstructions and analyzing a larger group of original plates.

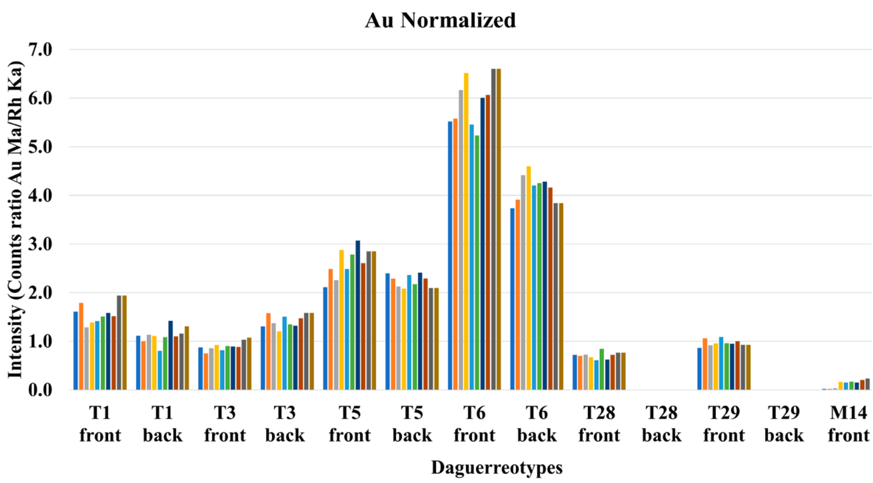

Figure 3. Histogram of the Au counts calculated for the Mα line, normalized to the Rh Kα, for ten XRF spectra each, recorded on the front and back of daguerreotypes T1, T3, T5, T6, T28, and T29. On the far right are the Au counts for the front side of the reconstructed daguerreotype M14

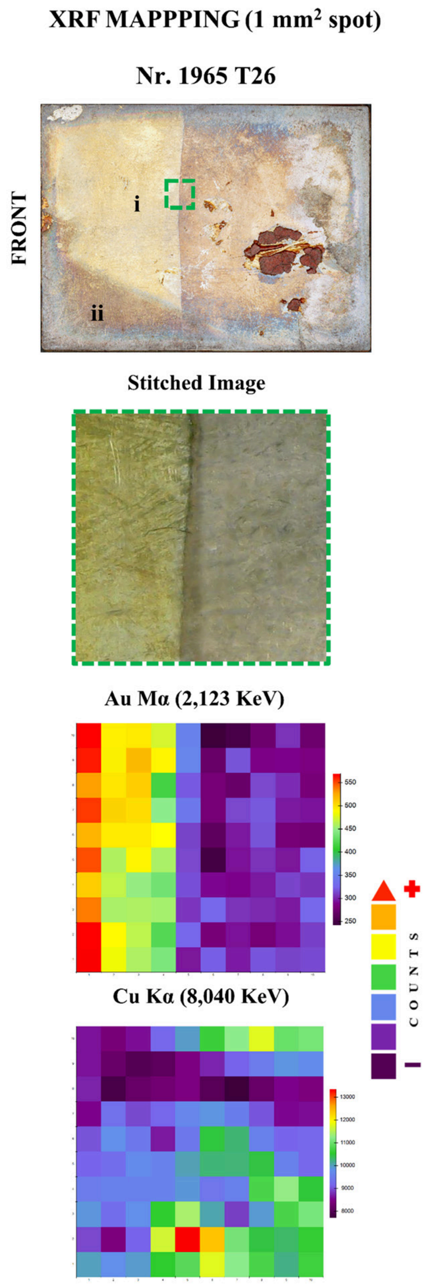

Figure 5. (Top) Visible image of the front of plate T26; the green square depicts the area of XRF mapping; (middle) the analyzed area; (bottom) XRF mapping of the integrated counts of the Au Mα line and Cu Kα lines

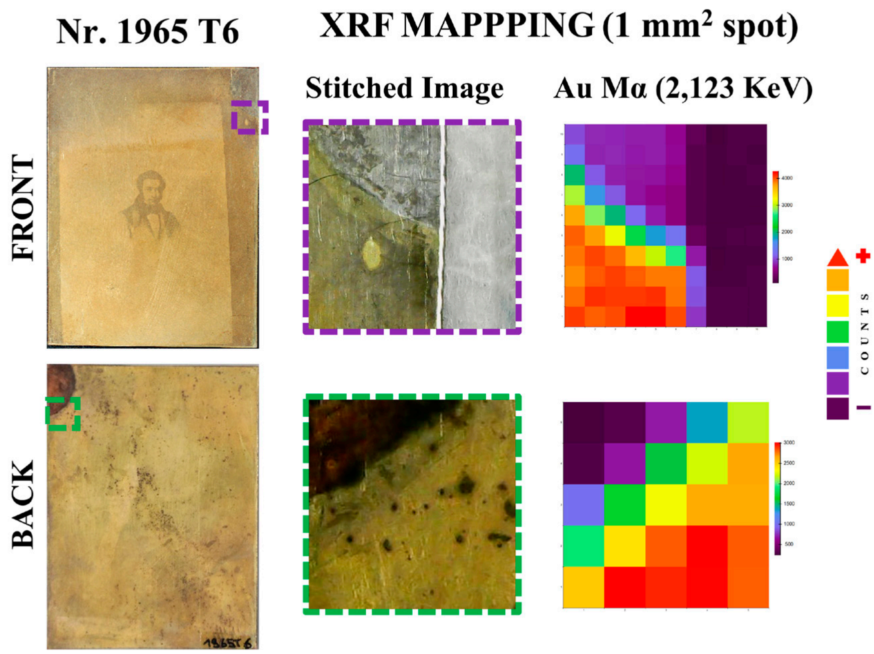

Figure 4. (Left) Visible images of the front (top) and back (bottom) of plate T6; the violet and green squares depict the area of XRF mapping; (middle) the analyzed areas; (right) XRF mapping of the integrated counts of the Au Mα line

Experimental processes

Daguerreotype T26 stood out from the other plates in that it appeared to be purely experimental. The plate displayed no image; the left side was golden in hue and the right side was copper-colored. XRF analysis revealed the elements Ag, Cl, Hg, and Cu. It is unclear why Hg was detected on the front side of T26, which had no apparent visible image. This study could not clarify whether Steinheil's own experiments and/or past conservation treatments were the reason for this phenomenon. Au was detected on the left side, in regions with (i) and without (ii) a golden appearance, while Cu was detected on both halves (Figure 5).

A reddish substance, reminiscent of sealing wax, was stuck to the front of the plate; and the back displayed a distinct irregular gloss. UV-A and UV-C analysis showed weak fluorescence of two different organic substances (Figure 6). The coating on the back (c) and a drop at the top left corner of the front (a) were identified by ER–FTIR as shellac, and the reddish material on the front (b) was a diterpenoid resin, such as that of the Pinus species related to pitch/tar and colophony, based on matches with most FTIR assignments in the IRUG database (Price et al. 2009) and the literature (Colombini et al. 2005, Azémard et al. 2014, Martin-Ramos et al. 2018) (Figure 7). Colophony has previously been identified on electrotype plates made for printing purposes (Tobisch et al. 2020). Even though only these two organic materials were identified, the authors cannot exclude the contribution of cyanide to the UV-C fluorescence, either as a component of a previous conservation treatment in 1942, a residue from electrolytic gilding, or other post-processing (Daffner et al. 1996, Buzit-Tragni 2005, Lough 2015).

The lump of colophony (Figure 6, area b) is split down the center and appears as if it was originally applied to fix a wire to the surface of the plate, which would have connected it to the electrical circuit, as it was

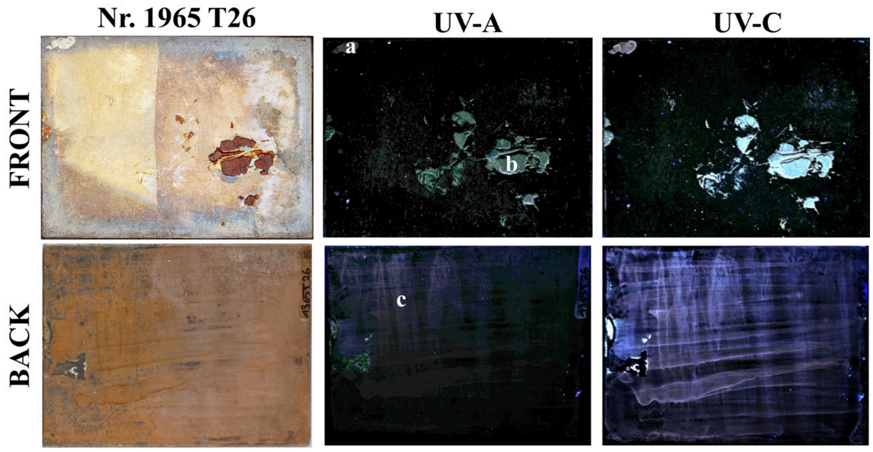

Figure 6. Plate T26. (Left) visible light; (middle) UV-A image; (right) UV-C image. (Top) Front of the plate. (Bottom) Back of the plate. The letters *a*, *b*, and *c* indicate the areas analyzed by ER–FTIR

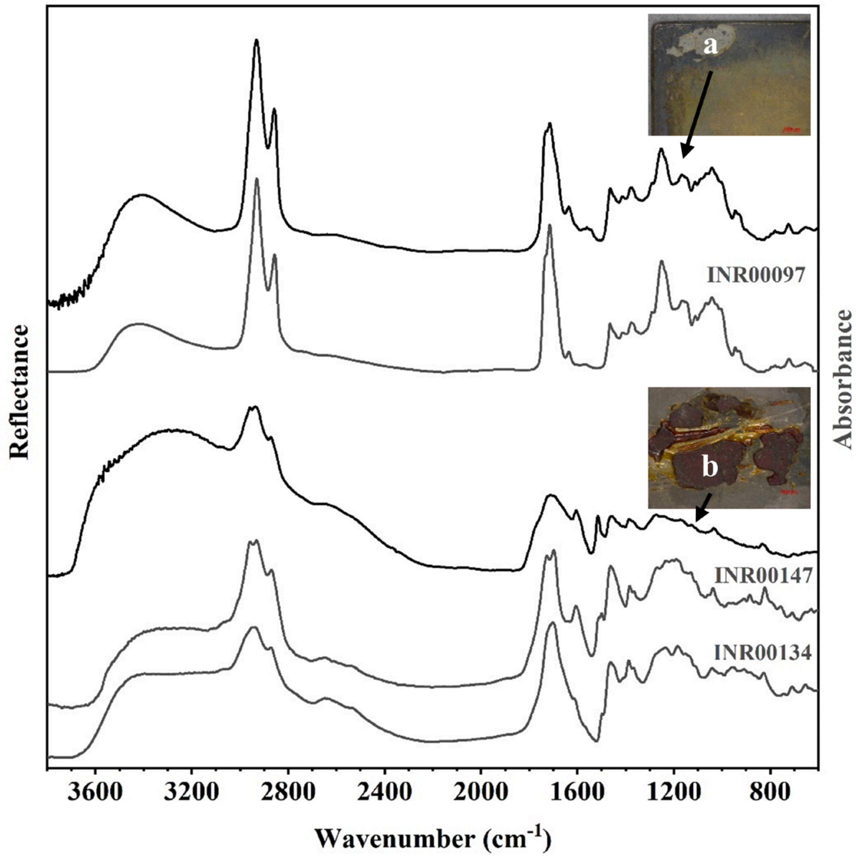

Figure 7. ER–FTIR spectra of the organic materials identified on plate T26 as shellac at area *a* (top) and diterpenoid resin at area *b* (bottom). Infrared spectra of reference compounds from the IRUG database are also shown for comparison: INR00097 shellac, INR00147 pitch, INR00134 colophony

hanging vertically in the electrolytic bath. The coated back would have been protected from Au deposition. It is not clear why plates T1, T3, T5, and T6 did not have obvious connection wire points, even if they might have been electrolytically gilded.

Electroplating daguerreotypes with copper

The organic substances on plate T26 remind us that Steinheil is said to have electrolytically coated his plates with a thin layer of copper.[4] The electroplating of the reconstructed daguerreotype M11 rendered the image

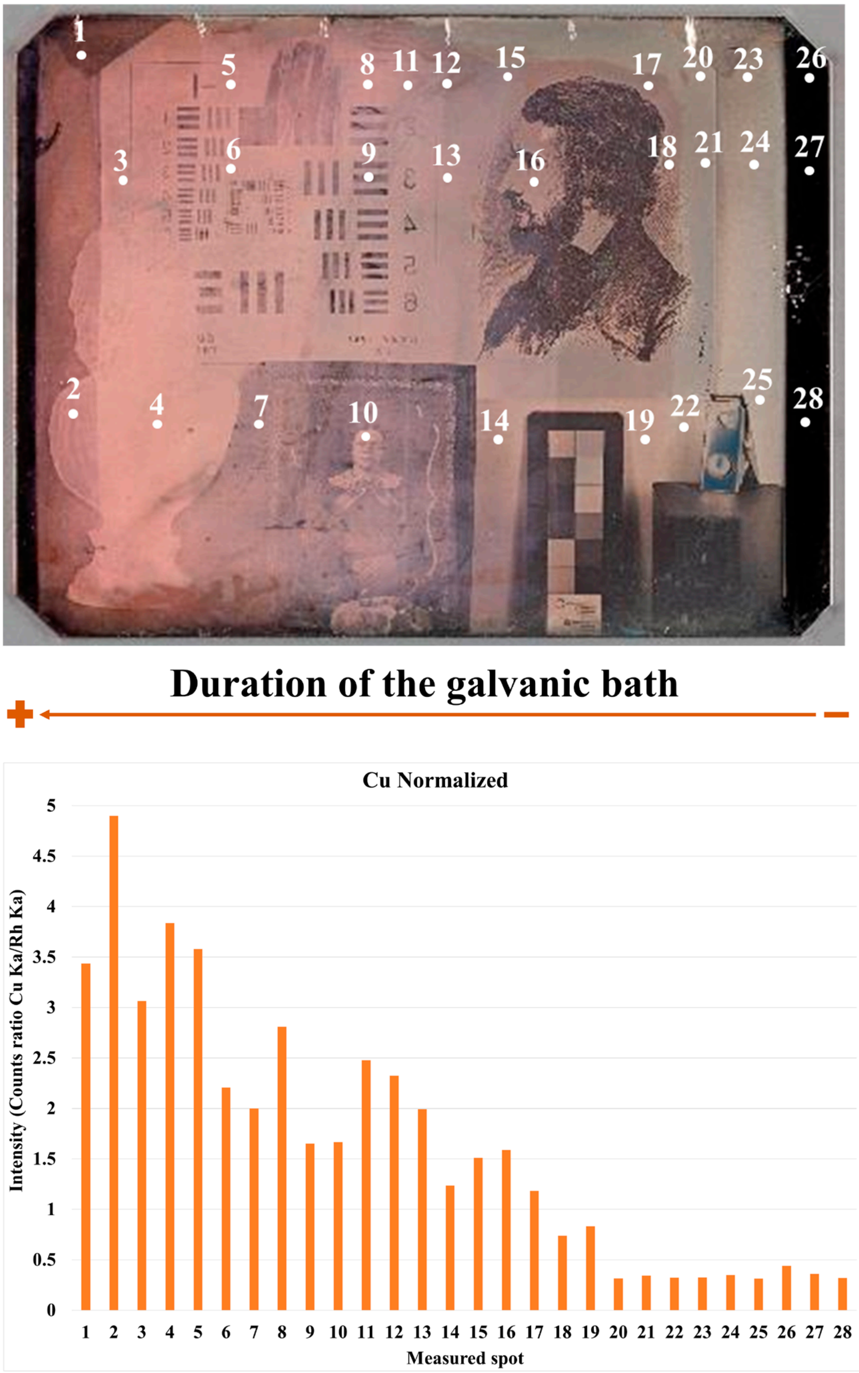

Figure 8. (Top) Modern reconstruction daguerreotype M11 with measured XRF spots. (Bottom) Histogram of the Cu counts (Kα line), normalized to the Rh Kα, for each spectra recorded from the electroplated surface. The plating duration increases from right to left resulting in an increasing copper layer thickness

rosy in tone (Figure 8), and a wipe test proved that even the thinnest copper coating protected the fragile daguerreotype image from physical abrasion. However, visual comparison of the 47 Steinheil plates with M11 showed that none of the original plates look like the modern one in terms of color and image quality.

CONCLUSION

In this study, the integration of information from historical sources, visual examination, and material analysis of a selection of Steinheil's daguerreotypes shed light on their production and processing methods. Technical analysis resulted in useful data, of which only the most representative results are presented here. There remain a number of unknowns, such as the nature of the restoration treatment the plates may have undergone in 1942. However, some conclusions can be made at this point.

Multivariate analysis was suitable in highlighting the broad variety of daguerreotype plates used by Steinheil. XRF easily detected copper, silver, and gold but could not help in determining whether Steinheil used accelerating halogen mixtures for sensitizing his plates. For the first time, this study examined electrolytic gilding of daguerreotypes as an alternative to Fizeau's chemical gilding method. XRF revealed that the Au signals found on the surface of the daguerreotypes varied significantly. While the warm-toned plates may have been chemically gilded, the plates with a more intense color, either on one or both sides, were probably electrolytically gilded. An extension of this study would involve reconstructing the processes and then expanding XRF analysis to a larger number of plates. This could help to determine discriminatory Au amounts specific to both methods.

Sources on Steinheil's practice hint at his experiments with electroplating daguerreotypes with copper, and the modern plate M11 gives an indication of the appearance and the resistance to physical abrasion that a copper-electroplated daguerreotype would have. However, neither visual nor instrumental analysis confirmed the presence of copper electroplating within the Steinheil collection.

Daguerreotypes are typically produced and processed without the use of organic substances. However, shellac and diterpenoid resin were identified in this study. Therefore, varnishes and waxes involved in the electrolytic processing call for more study, including the preparation of tailored reconstructions. This would result in more systematic research on the role of organic substances on daguerreotypes.

In general, it was found that the reconstruction of Steinheil's processes greatly helped in understanding the original objects, since the modern plates served well for visual and analytic comparison. However, since Steinheil's work was experimental, the reconstructions may not be accurate.

While this is the first time that Steinheil's daguerreotypes have been examined scientifically, only seven of the 47 daguerreotypes were discussed in this study, highlighting some aspects of Steinheil's work. The data collected from all of the plates will be used in ongoing research, in which multivariate analysis will combine different sources of information (elemental composition, subject, plate provenance, thickness, cut edges, etc.) to better understand the collection as a whole. Future work will also consider whether Steinheil was experimenting with electrotyping, as suggested by Trnkova 2021. In particular, the seven matte plates are unusual and require scanning electron microscopy (SEM) (Pilko 2017) to better understand their morphology and elemental composition. As such, this study offers a beginning point for future investigation of Steinheil's unique work at the dawn of photography in Germany, and it also helped in the planning of new conservation enclosures that will preserve this rare collection of daguerreotypes.

ACKNOWLEDGMENTS

The authors would like to thank Georgios Magkanas for sharing the Matlab scripts. The present work was carried out with the support of the Scholar in Residence Program of the Deutsches Museum (residency of Élia Roldão) and InsiTUMlab, funded by the German Research Foundation – Project n. INST/95/1722-1. The authors also thank the photographer conservator Marjen Schmidt for her input.

NOTES

[1] Kemp, Cornelia. *Licht – Bild – Experiment. Franz von Kobell, Carl August Steinheil und die Erfindung der Fotografie in München.* Deutsches Museum Abhandlungen und Berichte. Munich: Deutsches Museum (forthcoming 2023).

[2] Steinheil referred in 1841 to the use of mixtures made of "chlorine and bromine […], iodine and bromine" ("Chlor u. Brom […], Jod u. Brom") by three Austrian photographers: Franz Kratochwila, Johan August, and Joseph Natterer (Deutsches Museum, Archive, FA005/504, 12.1.1841-15.6.1842, lines 263–265).

[3] In a lecture at the Bavarian Academy of Sciences in Munich, Steinheil mentioned his "method of gilding by means of galvanic currents, which he first carried out here" ("Methode der Vergoldung mittels galvanischer Ströme, die er hier zuerst ausgeführt") on daguerreotypes (*Archiv der Bayerischen Akademie der Wissenschaften* (ABAdW), Protokolle, Vol. 58, 13.05.1842, p. 103).

[4] Steinheil reported in 1840 both at the Bavarian Academy of Sciences and Polytechnical Association on "an improvement in the representation of Daguerre's light images, and on the copper plating of the plated silver plates" ("eine Verbesserung in der Darstellung Daguerre'scher Licht-Bilder, und über das Verkupfern der platierten Silberplatten") (ABAdW, Protokolle, Vol. 55, 14.03.1840, p. 232).

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APPENDIX

Stereomicroscope images were taken with a Stemi508 (Zeiss) microscope coupled with an Axiocam105 color digital camera.

UV-A (366 nm) and UV-C (254 nm) examinations were made with a Bresemann+Schorpp UV-lamp following the protocol proposed by Barcella (2009) and Warda (2011).

ER–FTIR measurements were carried out using an ALPHA spectrometer (Bruker Optics). The spectral range investigated was 4000–400 cm^{-1}, with 4 cm^{-1} resolution and co-added 64 scans. The software was Opus 8.1.

Scanning macro (MA)–XRF analysis was performed with an ELIO spectrometer (Bruker) equipped with an Rh source operating at 50 kV and 80 µA. The focal spot size was 1 mm, with an acquisition time of 180 s for punctual analysis and 5 s/px for mapping. The spatial distributions of the elements were obtained using Bruker software. Neither helium flow nor filters were used.

Semi-quantitative data evaluation was performed with ArtTAX-Ctrl software (Intax). PCA was applied using a PLS_Toolbox (Eigenvecton Research) running on MATLAB R2022a. The data were mean-centered and pretreated by applying a standard normal variate (SNV) algorithm (Burns and Ciurczak 2007).

To cite this article:
Angelin, E.M., C. Sessa, M. Jürgens, E. Roldão, C. Kemp, and M. Pamplona. 2023. Carl August Steinheil's pioneering daguerreotypes: Nondestructive investigation of his production and processing methods. In *Working Towards a Sustainable Past. ICOM-CC 20th Triennial Conference Preprints, Valencia, 18–22 September 2023,* ed. J. Bridgland. Paris: International Council of Museums.