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Monitoring the photographic process, degradation and restoration of 21st century Daguerreotypes by wavelength-dispersive X-ray fluorescence spectrometry

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This study applied wavelength-dispersive X-ray fluorescence spectrometry (WDXRF), with its high spectral resolution, to monitor the photographic process, tarnishing and restoration of pristine Daguerreotypes made in the traditional 19th century fashion. The elemental changes upon restoration *via* thiourea treatment, were evaluated and compared to a method based on bulk electrolysis. The WDXRF system was found to successfully resolve all lines of interest including in the mercury-bromine-gold region. Sulfur, one of the main components of tarnish, was removed efficiently from the surface of the Daguerreotype when restored by electro-cleaning. Restoration by thiourea immersion removed sulfur from the surface of the Daguerreotype to a point at which the residual sulfur was equivalent in content to the residue left after gilding (*i.e.* from thiosulfate). Thiourea treatment was found to remove a significant amount of gold from the surface of the Daguerreotype, which may explain the sometimes observed dullness imparted to the Daguerreotype after restoration with thiourea. Also, Daguerrian measles were found to accumulate on thiourea treated plates *versus* those cleaned by electro-cleaning which ultimately negatively imparts further artefacts to the image after restoration.

1. Introduction

The 19th of August 1839 marked a remarkable day in the history of photographic arts. On that day, Louis Jacques Mandé Daguerre presented his invention to the world: the first known method of producing photographs.[1] The method, as described in Daguerre's manual, is based on the formation of an image on a halide sensitized silver surface and pointed the way to the production of the silver halide-based films so familiar to this day. Daguerre's original process for producing images was conceptually simple: a silver surface was highly polished, the polished silver surface was sensitized with iodine vapour forming a light sensitive silver iodide layer, the sensitized plate was exposed to the object to be imaged for a determined length of time, the plate now containing the latent image was exposed to mercury vapour until the image was developed and then the image fixed by treatment with a concentrated solution of common salt (NaCl) or a solution of sodium thiosulfate. The result was a photographic image (a Daguerreotype), which to this day has unsurpassed tone quality and resolution (Fig. 1). Several modifications were later made to the original process including the use of other halides during sensitization (bromine and chlorine) which were found to increase the photosensitivity of the plate by *ca.* 60 times, significantly reducing the exposure time. Another change to the original process was gilding of the Daguerreotype, where the plate was treated with a solution of gold chloride and thiosulfate resulting in increased durability and enhanced brilliance of the image.[1,2] Given that Daguerreotypes are unique and irreproducible objects and that certain collections hold historically valuable images, restoration of Daguerreotypes has become an active area of research within the restoration science community.

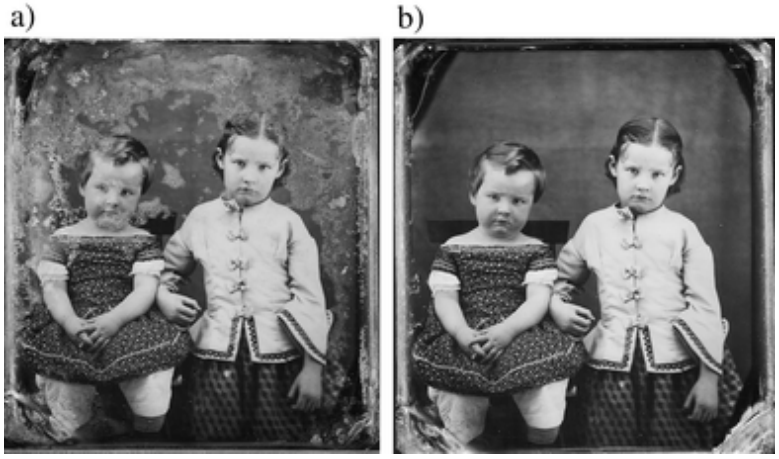

Fig. 1 (a) Nineteenth century Daguerreotype demonstrating tarnish which obscures part of the image; (b) image (a) after restoration by electro-cleaning (M. Robinson, Century Darkroom) demonstrating the brilliance and outstanding tone quality of the image. Images used with the permission of Mike Robinson, Century Darkroom, Toronto, Ontario, Canada.

The main issue regarding the conservation of Daguerreotypes has been the formation of tarnish on the surface, which can obstruct the view of the image (see Fig. 1a). The tarnish is generally regarded as being due to the formation of silver sulfide through reaction with atmospheric gases; however, several studies have shown the presence of other elements, including traces of oxygen, chlorine, carbon, nitrogen, silicon, potassium, sodium and calcium, as well as aromatic organic compounds at tarnish sites.[1–5]

The traditional Daguerreotype enclosure is itself an environment that allows for the accumulation of degradation products from the casing (*i.e.* brass mats and other case parts) which is in close proximity to the image, and is presumed to enhance deterioration of the image over time.[1–3] Other deterioration artefacts are not due to reaction with atmospheric gases or by-products of casing deterioration, the most notable being the so-called "Daguerreian measles,"[1] which appear as black specks on the images. "Measles" are assumed to be precipitated elemental sulfur from the decomposed thiosulfate in the gilding or fixing solutions, and a by-product of thiourea tarnish removal treatment.

The history of Daguerreotype restoration contains several examples of "cleaning" treatments that resulted in catastrophic damage to the images. A number of historically important Daguerreotypes have been lost due to treatments with cyanide and thiourea. Particle loss, etching of the surface and an observed dullness on gilded plates following treatment have been observed.[1] The dullness observed after thiourea treatment of gilded plates has led to the belief that gold may be removed during treatment as gilding enhances the brilliance of the image.[1,6–8] Although mild solutions of ammonia and detergents have been used for the removal of tarnish with various degrees of success, the most popular restoration agent since the 1950s has been thiourea.[1,9] More recently, electro-cleaning techniques have been introduced and investigated as a means of removing the tarnish from the surface of gilded Daguerreotypes as electro-cleaning may allow for better control over the process.[1]

Swan and co-workers[2] and Barger and White[1] have attempted to study elemental changes at the surface of the Daguerreotype after deterioration and thiourea restoration; however, questions still remain as to whether thiourea is an effective and safe method of restoring Daguerreotypes. Swan *et al.*,[2] using scanning-electron microscopy energy-dispersive X-ray fluorescence spectrometry (SEM-EDX), have postulated the crystalline phase and chemical formula for the mercury-gold amalgam image particles, although this work has been disputed by Barger and White.[1] Swan *et al.*[2] have also concluded, based on SEM-EDX and electron microprobe analysis, that gold is distributed evenly along the plate, while Barger *et al.*[10] and Barger and White[1] contend that the gold is unevenly distributed along the surface of the Daguerreotype with higher concentrations in areas with a high image particle density. Despite these studies, the chemical nature of the Daguerreotype is still unclear and its study hindered by the fact that only antique Daguerreotypes with unknown conservation history are typically available for study. The confounding factor that several elements may have been introduced to the surface during an undocumented conservation effort also cannot be ignored.

Energy-dispersive X-ray fluorescence spectrometry (EDXRF/EDX) has been used extensively because it allows for surface micro-analysis; however, the fact that certain elements of interest to Daguerreotypes (*i.e.* gold, bromine and mercury) have X-ray lines that are so close in energy that a standard EDXRF system, based on detection by a Si(Li) or silicon drift detector (SDD), cannot adequately resolve them; therefore, certain conclusions regarding the elemental content on Daguerreotype surfaces remain ambiguous.

This work presents an observational study of the elemental history of Daguerreotypes throughout the processes of plate preparation, photographic development, accelerated ageing/tarnishing and restoration by thiourea treatment, with a brief comparison to an electro-cleaning method, using a wavelength-dispersive X-ray fluorescence (WDXRF) system on pristine and freshly prepared gilded and ungilded Daguerreotypes, with known conservation history. Wavelength-dispersive XRF has sufficient spectral resolution and sensitivity to monitor the elements of interest more accurately than in previous studies based on EDXRF systems, as WDXRF can easily resolve X-ray lines with resolutions on the order of a few electron-volts superior to the resolutions common to EDXRF systems.

2. Experimental

2.1 Preparation of Daguerreotypes

All Daguerreotypes were prepared specifically for this study by Century Darkroom, Toronto (Daguerreotypist, Mike Robinson) as (2 × 2) cm squares with three quadrants prepared with tones of highlight, mid-tone and shadow and a forth as an index to be measured (Fig. 2). The method of preparation followed the traditional methodology based on the work of Humphrey.[11] The Daguerreotype substrate was specifically prepared by the traditional clad rolling process which, combined with the traditional method of Daguerreotyping, was aimed at mimicking pristine Daguerreotypes equivalent to those prepared in the 19th century and encountered by conservation scientists today. The substrate consisted of a clad silver plate with a thickness of copper of 482 μm and a silver thickness of 16–25 μm. The Daguerreotypes were all prepared from a single full plate of substrate to ensure homogeneity of the images and were cut to size after the entire process of Daguerreotyping was completed.

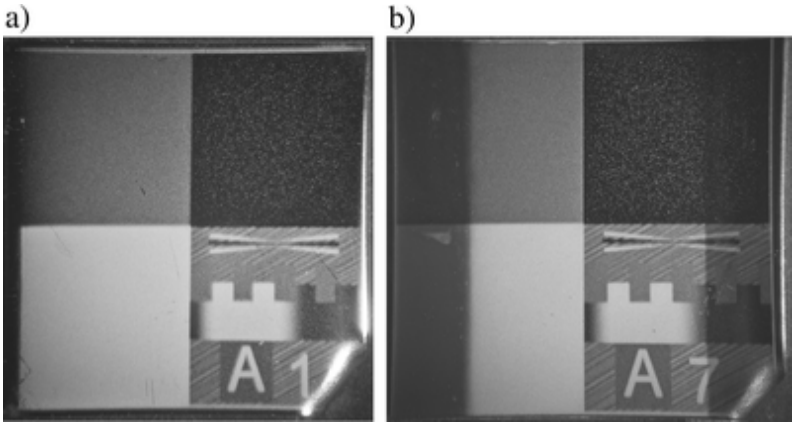

Fig. 2 Daguerreotype samples used in this work as prepared by Century Darkroom. (a) an untarnished, ungilded Daguerreotype and (b) an example of a tarnished Daguerreotype after accelerated ageing using traditional brass contacts. The Daguerreotypes were prepared with dimensions of (2 × 2) cm and weighed approximately 2.5 g. The Daguerreotypes were prepared with tones of (from bottom left-hand corner to upper right-hand corner) shadow, mid-tone and highlight.

Sensitization of the polished plate was performed with an iodine and bromine mixture. The sensitized plate was used to acquire the image, the image developed with mercury vapour and the image fixed by application of a solution of 1.6% w/v sodium thiosulfate pentahydrate followed by several washings with water.

Gilding, when specified, was performed by treating the surface of the plate (now containing the developed and fixed image) with a buffered gold solution containing a reducing agent. The gilding method proceeded by preparing a *Part A* solution of 0.2% w/v $HAuCl_4{\cdot}xH_2O$ in distilled water. The solution was tested with pH test paper and was found to generally have a pH of approximately 2–2.5. A 2% w/v solution of sodium metaborate anhydrous was added drop-wise until the pH was raised to 4–5. A *Part B* solution was prepared by dissolving 1.6 g of sodium thiosulfate pentahydrate in distilled water to make a *Part B* solution of a final volume of 100 mL. This *Part B* solution was added slowly to 100 mL of *Part A* solution with agitation for a final total volume of 200 mL. Gilding was performed with solutions that were prepared fresh as well as a solution allowed to age for several weeks (Table 1 for indexing). This solution was added directly to the plate surface at a minimum volume to cover the surface of the plate and form a meniscus. The plate was lightly heated with an alcohol lamp for a period necessary to produce an image with a brilliant character (*ca*. 60 s). The plate was washed thoroughly with water and dried with heated air prior to analysis or further treatment.

Table 1 Daguerreotype index and corresponding treatment used throughout this study.

Bare plates		Imaged plates	
N-UP	New plate with observable tarnish, unpolished	NRS	Plate used to prepare image, N-P (above)
T-UP	Old plate with observable tarnish, unpolished	RS	Plate used to prepare image, N-P-RS (above)[a]
N-P	New plate polished as described	NRS-T	Plate used to prepare image, T-P (above)
T-P	Old plate with observable tarnish, polished	UG	Ungilded
N-P-RS	New plate, polished and re-silvered[a]	G1	Gilded with a fresh toning solution made the day of Daguerreotype preparation
		G2	Gilded with an old toning solution, (sulfur precipitation evident)
		A	Accelerated aging
		EC-50	Electro-cleaned at 50 mA
		EC-75	Electro-cleaned at 75 mA
		TU-S	Thiourea immersion treatment for a short *ca*. 30 s wash
		TU-L	Thiourea immersion treatment for a 5 min wash

[a] For re-silvering methodology see the work of Humphrey.[11]

Accelerated aging was performed by immersion of the plates in an aqueous solution of sodium sulfide prepared to a concentration of *ca*. 2 g L^{-1} prepared from undried sodium sulfide. To simulate a traditional Daguerreotype casing, traditional brass mats were placed along the edge of the plates (the result is shown in Fig. 2b after tarnish with the use of the brass mats). The aging process was performed for a period of time required until the first sign of tarnish was present.

Restoration by thiourea immersion was performed by immersion of the tarnished plate in a solution of thiourea prepared as prescribed by Newhall.[12] The solution was prepared by mixing 70 g of thiourea with 60 mL of 85% w/w phosphoric acid. The entire mixture was then brought to a final volume of 1000 mL with water. Restoration using this solution was performed by immersion followed by either a brief (*ca*. 30 s) or a 5 min wash in distilled deionized water. Electro-cleaning was performed by Century Darkroom, Toronto under two currents of 75 mA and 50 mA. The electro-cleaning method was a modification of that described by Barger and White[1] in which the Daguerreotype was placed into alternating basic (1% w/v sodium metaborate) and acidic (0.3% w/v citric acid) solutions with variation of current to alternate the Daguerreotype as being the anode or cathode of the system (contained in a stainless steel housing). All Daguerreotypes under study, their treatment and their indexes used throughout this work are listed in Table 1.

Table 2 Optimized experimental conditions for the elements monitored in this study by WDXRF. LiF(200) refers to lithium fluoride (200) and PET to pentaerythritol. The detector systems are abbreviated: SPC = sealed proportional counter (Ar/CH_4), SCINT = scintillation counter (NaI)

Element	Crystal	Line	Collimator/°	Detector	Tube voltage/kV	Tube current/mA
Fe	LiF200	Kα1	0.23	SCINT	50	20
Cu[a]	LiF200	Kα1	0.23	SCINT	50	20
Ag	LiF200	Kα1	0.23	SCINT	50	10
Au	LiF200	Lα1	0.23	SCINT	50	20
Hg	LiF200	Lα1	0.23	SCINT	50	20
S	PET	Kα1	0.46	SPC	27	37
Cl	PET	Kα1	0.46	SPC	27	37

Br	LiF200	Kα1	0.23	SCINT	50	20
Br (alternate)	PET	Lα1	0.23	SPC	27	37
I	LiF200	Kα1	0.23	SCINT	50	20

[a] Cu line measured with a 500 μm Al primary filter to void out system contamination.

2.2. X-ray spectrometry

Elemental analysis of the Daguerreotypes was performed using an S4 Explorer wavelength-dispersive X-ray fluorescence spectrometer (Bruker-AXS, Madison, WI). The spectrometer was equipped with a rhodium X-ray tube of 1 kW maximum power (maximum tube voltage and current of 50 kV and 50 mA adjusted to maintain 1 kW maximum power) (Table 2). Daguerreotypes were prepared to fit directly into a sample cup with an 8 mm mask to control the overall area irradiated. The Daguerreotypes were of sufficient weight (*ca*. 2.5 g) that no movement was observed during the automated sampling. The count rate for each of the elements studied was measured for the sample cups containing a pure graphite blank and the instrumental drift evaluated periodically with a series of standard glasses (Lot: 134-28, Breitländer, Germany). The intensities emitted from the sample cup/graphite blank were subtracted from each measurement made in the respective sample mask after suitable background subtraction. No significant contribution for any element was observed from the sample cups/masks except for gold. The gold signal from the cup did not exceed (15 ± 2)% of the signal observed for each of the gilded samples. The elements measured and the scanning/operating conditions are listed in Table 2. All preliminary analyses were performed using the SpectraPlus® software (v.1.7.2, Bruker-AXS, Madison, WI) associated with the spectrometer in which net intensities were acquired from full spectral scans in order to compensate for line overlaps and for the calculation of background intensities. The elements that were present above the instrumental detection limits, as determined by full spectral scans of the plates are listed in Table 2. Experimental scans were acquired at a scan rate of 30 s per channel. The Hg/Au/Br region was decomposed using spectral curve-fitting based on the method of Marquardt[13] with a model based on an appropriate polynomial background and simple Gaussian response function. All measurements were made in triplicate.

2.3. Electron microscopy

Scanning Electron Microscopy was performed on a JEOL, model JSM-6380LV, instrument using a tungsten filament as the electron source. The sample chamber was under vacuum at about 10^{-5} torr. Acceleration voltages (5 kV or 20 kV) are listed on all figures as appropriate.

3. Results and discussion

3.1. Changes to the bare substrate and the effects of polishing

Daguerreotyping begins by selection of the silver substrate on which the image is formed. Traditionally, the plate of choice consists of a copper backing onto which a layer of silver is bonded using the cold-roll cladding process. As the technology evolved, electro-deposited silver became common. Both plate selections are of interest to the conservator as there are plentiful examples of both, and they are often indistinguishable in practice.

The variations observed in the silver signal/content (Fig. 3) are considered to be due to the polishing, which is performed manually. Manual polishing is probably responsible for the inhomogeneity in silver signal as evaluated from the large standard deviations in signal measurements, as this standard error cannot be accounted for by counting statistics alone. Because of the inhomogenity of the silver substrate layer, the ability of WDXRF to monitor small changes in the silver content on the surface/plate due to image formation was hindered, as the observed net silver signal is a combination of the silver in the silver/mercury amalgam image particles and the substrate.

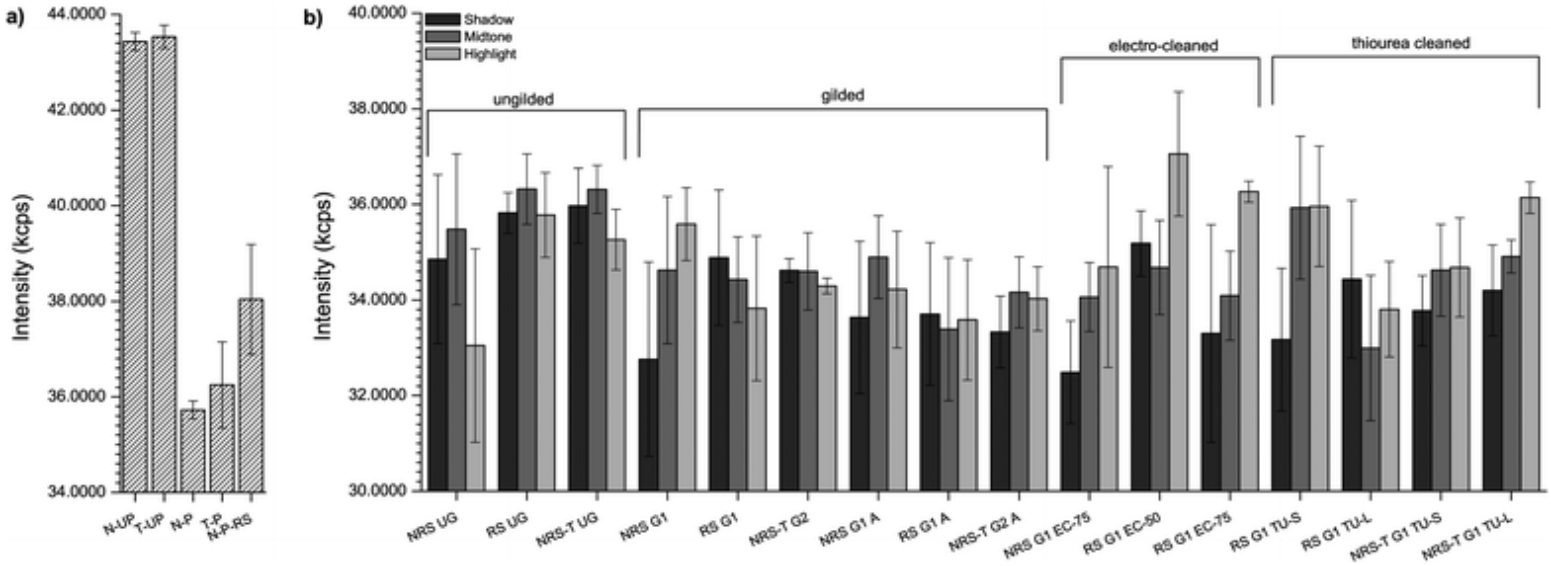

Fig. 3 Intensity of the silver $K\alpha_{1,2}$ (λ = 0.561 Å) line for (a) various bare plates (b) various treatments (indexes listed in Table 1). The error bars represent the variation between three independent samples taken from the sample plate.

The silver substrates used in this study, and traditionally, are thin films of silver (16–25 μm) on a copper backing (482 μm) in which the silver layer does not fulfill the condition of infinite thickness, that is, a thickness in which the variations in thickness would result in no change in observed X-ray line intensity. In this case, variations in the silver thickness would be expected to be accompanied by a change in X-ray intensity proportional to the exponential of the thickness change which may account for the large variations due to inhomogenities in this layer's thickness.[14] Mantler describes the theoretical basis for the X-ray emission from multilayer systems.[14] In regards to the Daguerreotype, although Mantler's expressions[14] indicate that the measured fluorescent intensity for silver is a function of the composition and thickness of all layers, the photographic layer (*i.e.*, that containing all image particles and any residual elements from the photographic process) and that of gold are estimated as sufficiently thin (on the order of several hundred nanometres) that any attenuation effects can safely be neglected. This is only an approximation as this photographic layer is composed of small particles (Fig. 4). As such, no real attenuation effects were considered and the intensity of the X-ray lines from elements in this region was assumed to be linearly proportional to the density and that these assumptions held throughout this work.

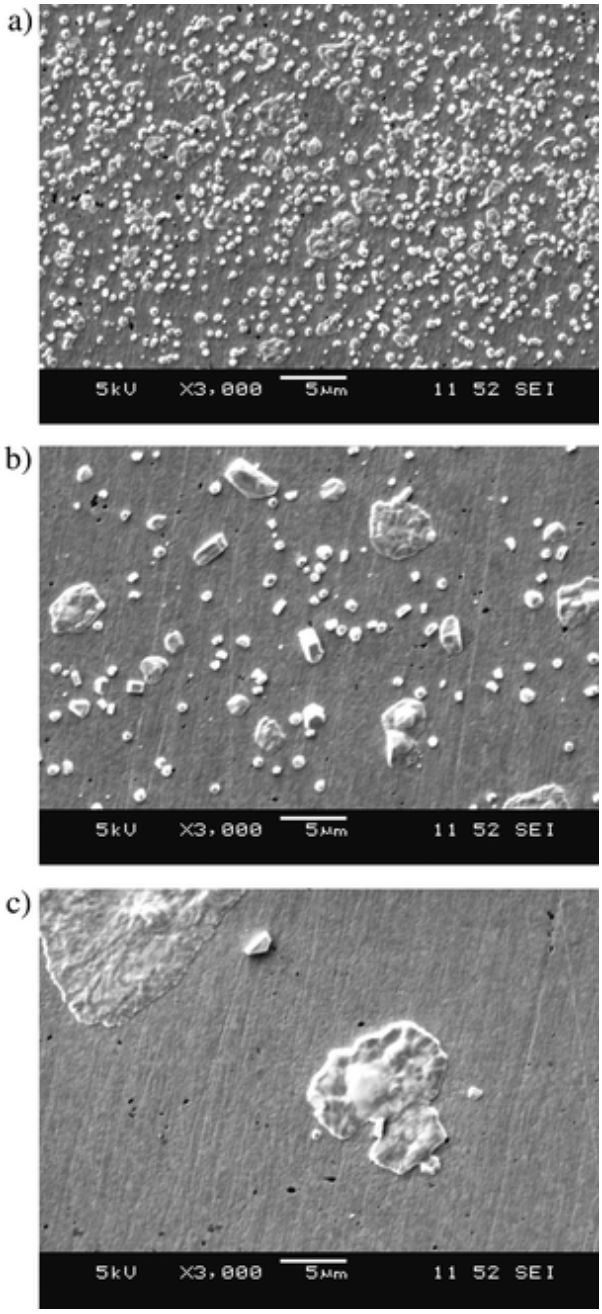

Fig. 4 Scanning electron microscopy images of the Daguerreotype image particles for various tones: (a) highlight (b) mid-tone (c) shadow.

The copper Kα/Kβ ratio is also a function of the thickness of the silver layer (Fig. 5) because the mass attenuation coefficient for the Cu Kα is greater than that of Kβ ($\mu/\rho_{K\alpha}$ = 214 cm^2 g^{-1} and $\mu/\rho_{K\beta}$ = 162 cm^2 g^{-1}, Ag as absorber);[15] therefore, the Kβ line would be expected to decrease less than the Kα for the same increase in silver thickness.[14] This is reflected in the decrease in the Cu Kα/Kβ ratio on polishing; the re-silvered plate is also re-polished which results in a similar Kα/Kβ ratio as the polished non-resilvered plate (Fig. 5). The copper signal itself is a combination of the signal from the copper backing and surface copper deposited during tarnishing from the brass mat contacts (a traditional component of the Daguerreotype plate package). Because the variation of the copper signal is highly dependent on small changes in the silver thickness, no apparent difference was observed for the copper signal after tarnishing in the presence of brass contacts, although copper has been shown to be present at the surface of tarnished Daguerreotypes by electron probe techniques and electron-induced EDXRF which is a more surface-specific technique than WDXRF.[2]

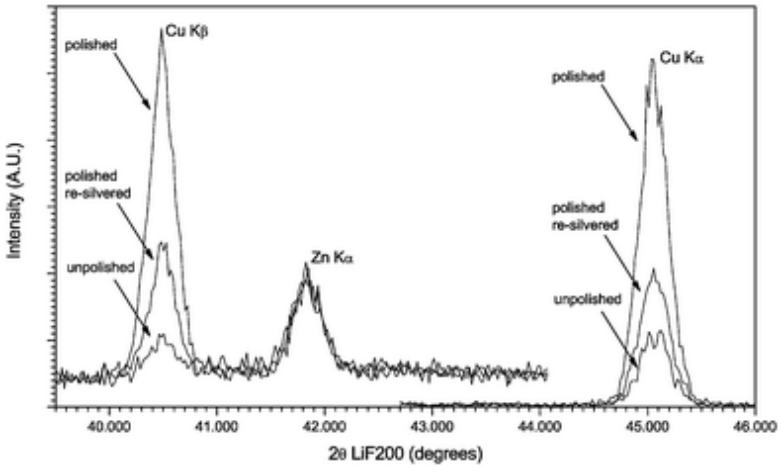

Fig. 5 Copper signal for different plate preparations. The Cu Kα /Kβ ratio changes slightly due to changes in the overall thickness of the attenuation silver layer (Kα/Kβ: polished = (0.96 ± 0.02), polished re-silvered = (0.99 ± 0.03), unpolished = (1.89 ± 0.05), $p < 0.05$). The zinc signal is due to inherent system contamination/background and not due to any zinc deposition on the plate as determined on a pure graphite blank.

The iron signal observed for the new, unpolished, plate (N-UP) is equivalent to that expected from the instrumental iron background (Fig. 6). The polishing seems to impart some iron to all of the plates. No apparent difference in iron content between plate preparations or restoration techniques was observed (Fig. 6, $p > 0.05$). Re-silvering by electroplating (N-P-RS) does not remove any of the residual iron, and neither does gilding or application of conservation methods (*i.e.*, thiosulfate or electro-cleaning, Fig. 6).

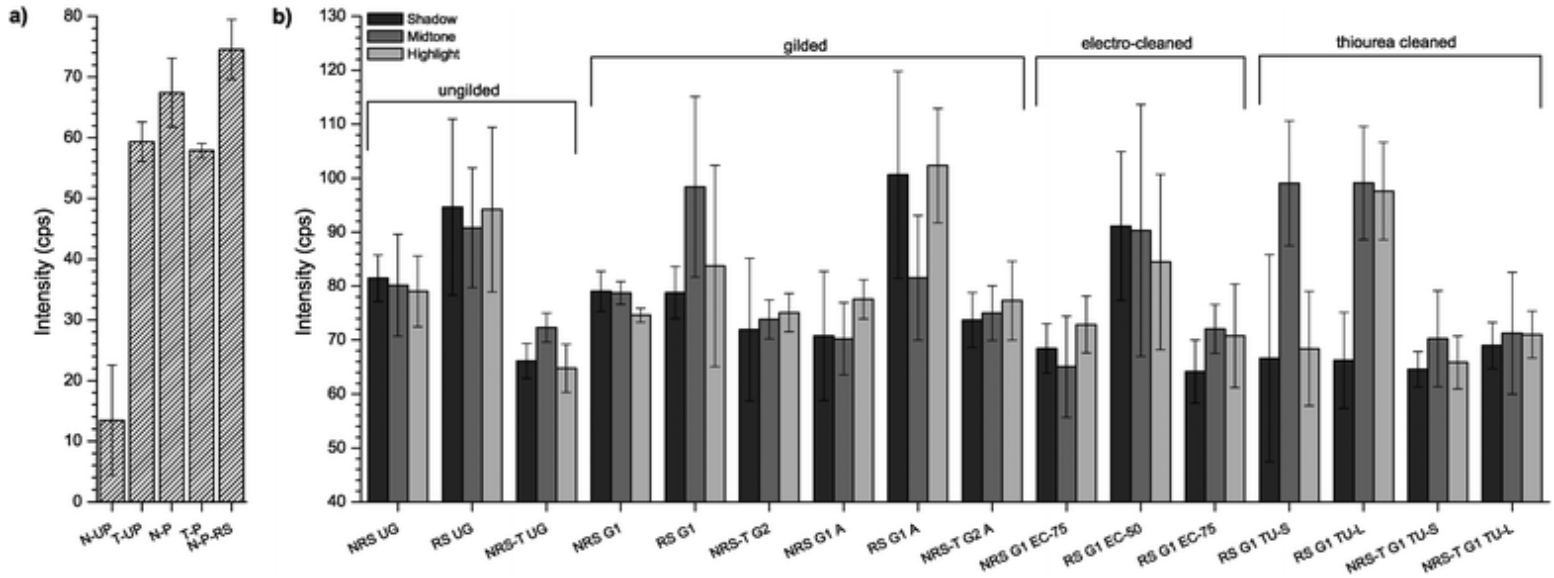

Fig. 6 Intensity of the iron K$\alpha_{1,2}$ (λ = 1.937 Å) line for (a) various bare plates (b) various treatments (indexes listed in Table 1). Note that iron is a natural system contaminate and has not been corrected for. The signal is constant between plates and is shown in the new unpolished plate (NUP) to have a signal of approximately 13 cps.

3.2. Influence of gilding and conservation on the image particles

It is important to determine if the mercury content of the plate changes after conservation. Such alterations in chemical composition would indicate changes to the image itself. While XRF is not able to distinguish between the silver in the image particles and the silver from the substrate, the mercury intensity can be used to provide an indication of changes to the image particles. Fig. 7 shows no changes in the mercury content after treatment by any method. The differences seen in Fig. 7 are probably due to variability in the Daguerreotyping process. Slight changes in the photographic and development process, including variations in lighting and the temperature of the mercury bath, cause differences in the mercury content

on the surface. There is no evidence to suggest that gilding or either of the conservation treatment methods cause any damage to the image ($p < 0.05$).

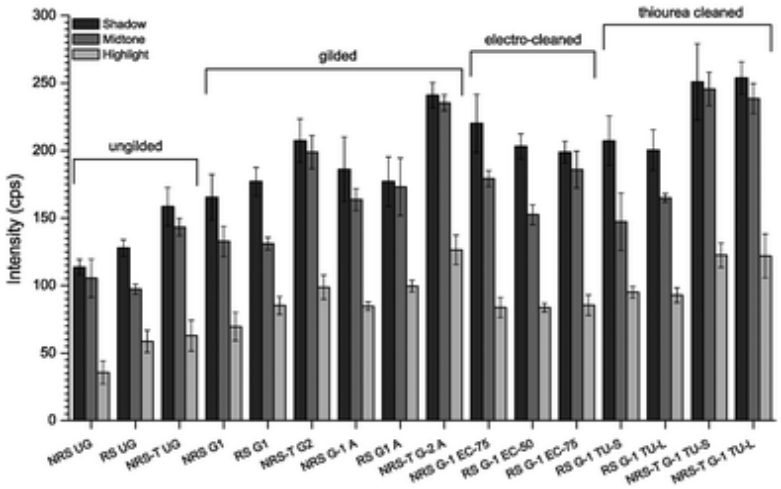

Fig. 7 Intensity of the mercury Lα_1 (λ = 1.242 Å) line for various treatments (indexes listed in Table 1). The variation between treatments is deemed due to variations in the photographic and development process and not due to damage or change caused by restoration.

The mercury content within a given image increases as highlight < mid-tone < shadow. The amalgam particles for the three image regions are shown in Fig. 4. The highlight regions contain particles that are small (<1 μm), numerous and crystalline in appearance, while the shadow particles are large (>5 μm), few in number and have the appearance of a core particle, surrounded by a puddle, presumably of mercury. However, the two types of particles are not exclusively seen in either area: some particles in the highlight and mid-tone regions have the appearance of those formed in the shadow, and some crystalline particles are seen in the shadow region.

Daguerreotype chemistry begins with the formation of AgX(ad) on the silver surface, where X = Br or I, depending on the vapour used to sensitise the plate. On exposure to light the photosensitive AgX becomes an excited, reactive species (AgX*), which is the nucleation site for formation of the mercury amalgam. Because less light falls on the shadow region, there will be fewer nucleation sites, and therefore fewer image particles, in the shadow areas. Mercury is introduced to the surface as a vapour, some of which adsorbs to the silver surface. The adsorbed mercury is mobile and moves about the surface until trapped at one of the nucleation sites. It seems from the images that there are two stages to the image particle formation: an initial stage, characterised by formation of an orderly solid, and a later stage during which a more liquid-like structure is formed. The shadow regions contain more of the latter particles because there are fewer nucleation sites and so each particle in the shadow traps more mercury atoms on average than those in the highlight or mid-tone regions. Overall, more mercury is trapped in the shadow region, despite the fact that there are fewer trap sites than in the mid-tone or highlight regions, suggesting that the liquid-like particles that form in the later stages of particle development are more effective at trapping mercury than are the crystalline particles formed in the early stages.

No halides (Cl, Br or I) were detected on the surface of the plates. Centano *et al.*[5] have reported the presence of chloride on the surface of Daguerreotypes as AgCl when using surface enhanced Raman spectrometry. The observed chloride might have been due to residual chloride from the gilding solutions. Barger and White's[1] EDXRF work appear to demonstrate chlorine content on the surface. However, the resolution of EDXRF systems is insufficient to distinguish between the silver Lℓ (λ = 4.707 Å) line and the chlorine Kα (λ = 4.728 Å) line. Bromine can also be misidentified due to its overlap with the Hg Lβ lines, as shown in Fig. 8. This region in the WDXRF spectrum however shows the absence of bromine after suitable fitting (Fig. 9). Further confirmation of the absence of bromine was provided by measurements using a PET analyzing crystal, with which there was no spectral overlap, and extended count times (10 000 s per channel). Under these conditions, no observable bromine signal over noise was detected (through the Br Lα line).

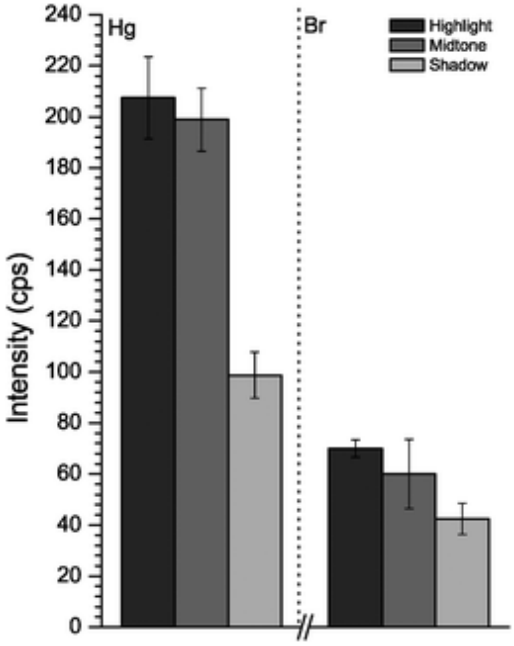

Fig. 8 Bromine intensity as determined by SpectraPlus® software associated with the WDXRF spectrometer. The general pattern is similar to that of the mercury pattern due to the simultaneous increase of the overlapping mercury Lβ lines.

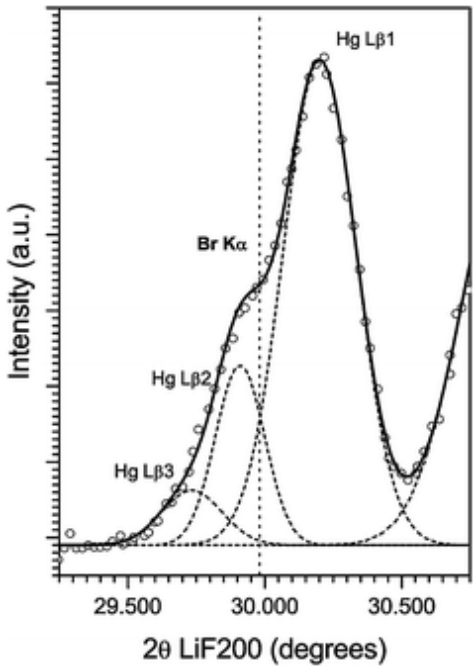

Fig. 9 Decomposition of the region encompassing the Br Kα lines and the Hg Lβ lines. There is no evidence to suggest any bromine on the surface of the plate including scans using an alternate crystal (PET).

3.3. Tarnishing and restoration

The major conservation and restoration issue surrounding Daguerreotypes is that they are prone to tarnishing. Tarnishing of the silver proceeds by reaction with H_2S naturally present in air.[1] To accelerate the process on the pristine Daguerreotypes created for this study, the plates were immersed in a sulfide solution with traditional brass contacts. The result was a marked increase in the sulfur content on the surface of the Daguerreotype (Fig. 10). Tarnish seems to accumulate

preferentially on the image particles due to sulfur's affinity for mercury (Fig. 11), suggesting that the sulfur precipitates as a mercury, rather than silver, species. As a consequence, the sulfur signal follows the same general pattern with image tone as mercury (highlight < mid-tone < shadow) (Fig. 7 and 10).

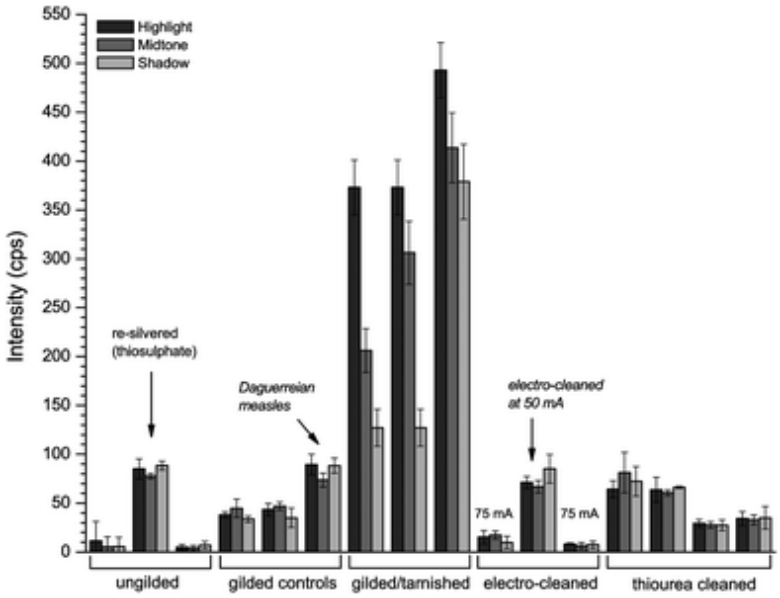

Fig. 10 Intensity of the sulfur $K\alpha_{1,2}$ line (λ = 5.373 Å) for various treatments. Although omitted for clarity, the indexes for the data follow that of all other figures.

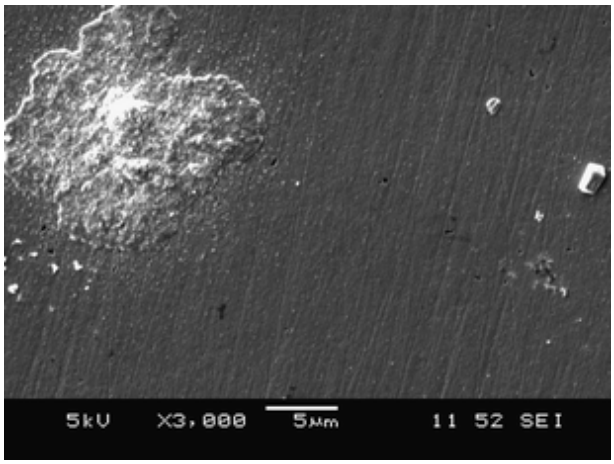

Fig. 11 Accumulation of tarnish particles on a shadow Hg/Ag amalgam shadow image particle.

Residual sulfur on plates that have been in contact with thiosulfate indicates that the thiosulfate itself may impart some sulfur that can contribute to tarnishing. From Fig. 10 it can be seen that the sulfur on the surface of the plate prior to accelerated aging is also slightly higher in the Daguerreotypes gilded with an aged solution of gold chloride ($p < 0.05$). The Daguerreotypes treated with an old solution of gold chloride all demonstrated signs of "Daguerreian measles,"[1] in which black, circular artefacts appear on the surface (Fig. 12). On historical Daguerreotypes such artefacts are thought to be due to thiosulfate reduction, which results in precipitation of a sulfur compound.[1] Plates treated with thiourea were also found to present Daguerreian measles while electro-cleaning was found not to form measles.

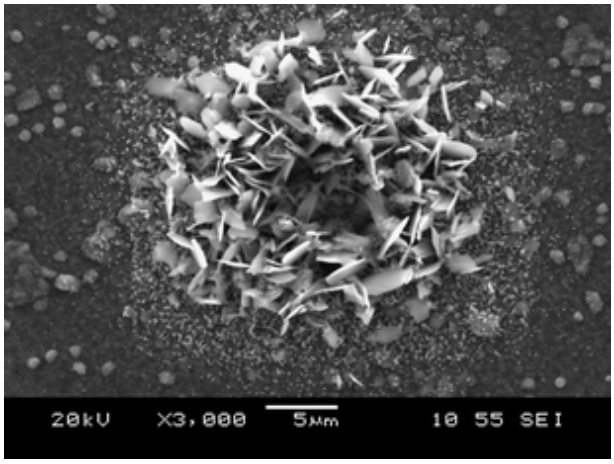

Fig. 12 An SEM image of a Daguerreian measle which appears on the surface of the Daguerreotype as a black circular artefact.

Electro-cleaning at high current (75 mA) effectively reduced the sulfur signal to a level about that of instrumental noise. Thiourea treatment and electro-cleaning at low current (50 mA) produced comparable results: The sulfur signal was reduced approximately to that of the surfaces exposed to thiosulfate during gilding. This result may indicate a two-step stripping process, in which the sulfur deposited from the sulfide solution during accelerated aging is removed first, followed by the sulfur deposited during thiosulfate reduction.

3.4. Restoration and its effect on image quality

Of particular interest to the Daguerreian community is the issue of gold stripping during tarnish removal. It has been observed that cleaning by thiourea causes a dulling effect on Daguerreotypes.[1] Since gold toning is used to strengthen the image and results in a more brilliant and aesthetically pleasing image, it has been postulated that the observed dulling effect is due to the treatment removing some gold. Analysis by WDXRF shows that thiourea treatment significantly decreases the gold content on the surface of the Daguerreotype while electro-cleaning does not (Fig. 13). The gold content is also homogeneously distributed across the bulk Daguerreotype surface as previously thought.[2] If gold were associated primarily with the image particles, its signal would be expected to follow the same pattern as mercury and sulfur (highlight < mid-tone < shadow).

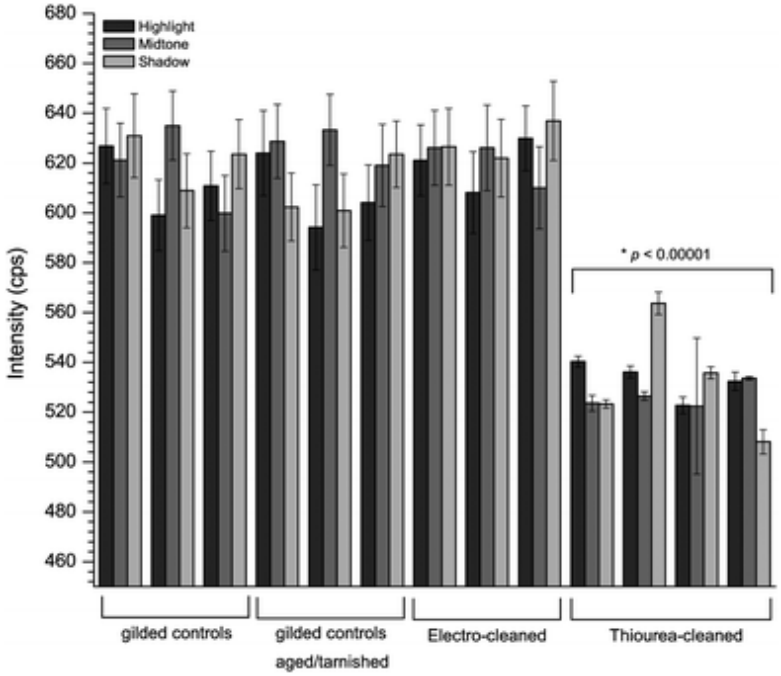

Fig. 13 Intensity of the gold $L\alpha_1$ (λ = 1.277 Å) line for various treatments. For all plates except the thiourea treatment plates, the gold content was found to be homogenous. Thiourea treatment

reduces the gold content on the surface of the Daguerreotype after a 5 min treatment. Although omitted for clarity, the indexes for the data follow that of all other figures.

4. Conclusions

With appropriate data analysis and curve fitting, WDXRF can successfully quantify intensities of all elemental lines of interest to Daguerreotype conservation, including mercury, bromine and gold. We found that iron accumulates on the plate after polishing, but does not seem to have any effect on the integrity of the Daguerreotype during aging or restoration. Mercury was distributed unevenly across the image: The mercury signal followed the pattern highlight < mid-tone < shadow, suggesting that the large, disordered particles of the shadow region were better scavengers of adsorbed mercury than the small, crystalline particles associated with the highlight regions. Sulfur showed the same pattern, suggesting that sulfur deposited during gilding and accelerated aging was associated with mercury, rather than silver. Mercury was not removed by treatment with thiourea or electro-cleaning. Sulfur was removed efficiently (near 100%) by electro-cleaning at 75 mA. Restoration by thiourea immersion or by electro-cleaning at 50 mA removed sulfur to a level equivalent to that after gilding (sulfur deposited by thiosulfate), suggesting a two-step removal process for sulfur. The gold signal was constant across the gilded image surface, independent of tone, suggesting that it does not associate preferentially with the particles, as sulfur and mercury did. Thiourea treatment removed gold from the surface, while electro-cleaning did not.

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