Synchrotron Radiation Analysis of Daguerreotypes: Surface Characterization, Electrocleaning, and Preservation

Madalena S. Kozachuk, The University of Western Ontario

Supervisor: Sham, Tsun-Kong, The University of Western Ontario
Co-Supervisor: Martin, Ronald R., The University of Western Ontario
Co-Supervisor: Nelson, Andrew J. & Coulthard, Ian. (The Canadian Light Source, Saskatoon, SK)

A thesis submitted in partial fulfillment of the requirements for the Doctor of Philosophy degree in Chemistry
© Madalena S. Kozachuk 2019

Follow this and additional works at: https://ir.lib.uwo.ca/etd

Part of the Analytical Chemistry Commons, Art and Materials Conservation Commons, and the Physical Chemistry Commons

Recommended Citation

This Dissertation/Thesis is brought to you for free and open access by Scholarship@Western. It has been accepted for inclusion in Electronic Thesis and Dissertation Repository by an authorized administrator of Scholarship@Western. For more information, please contact wlswadmin@uwo.ca.
Abstract

The first commercially viable photographic image, the daguerreotype, captured images from 1839 to 1860. While daguerreotypes provide a significant historical record of 19th century individuals and events, deterioration now disfigures many of these images. This work describes the application of synchrotron radiation (SR) to the study of daguerreotypes.

Three goals were addressed in this thesis: 1) to utilize SR to further elucidate the physics and chemistry of the daguerreotype and how the surface varies with time, 2) to study the effects of the electrocleaning system on the daguerreotype surface, and 3) to propose suggestions to improve their preservation and restoration efforts.

The collection of the Ag and Au L$_3$-edges from a daguerreotype test plate showed that the image particles on the surface form an alloy with a fcc structure and that the degree of Au diffusion into the Ag plate differed across the surface. This variation in diffusion produced an average alloy composition of $\text{Ag}_{90}\text{Au}_{10}$ (shadow and midtone regions) and $\text{Ag}_{73}\text{Au}_{27}$ (highlight region). Finally, both lab and SR sourced X-ray photoelectron spectroscopy showed Hg was present only within the first 1-2 nm of the surface and that alloying with Ag was possible but not consistent across all regions.

Expanding to 19th century plates, the primary tarnish on the surface was $\text{Ag}_2\text{S}$ and $\text{AgCl}$. X-ray fluorescence (XRF) found S and Cl to accumulate on high-density image particle regions. S K-edge suggested a possible Hg-S interaction, corroborating minimal amalgamation between Hg and Ag.

XRF of the eye region noted a variety of deterioration compounds and blemishes, which were removed when treated electrochemically by both the Barger (1982) and Wei (2011) methods. Full plate XRF imaging revealed that while the Hg L emission retained a great deal of information both before and after cleaning that Au and Hg were removed: the Barger method had the greatest impact on the relative concentrations of Au, while Hg appears to be removed in similar quantities by both the Wei and Barger process. Importantly, this work
presents a method that allows, for the very first time, the retrieval of fine daguerreotype images tarnished beyond recognition.

**Keywords**

Daguerreotypes, X-ray absorption near-edge structure, X-ray fluorescence microscopy, X-ray photoelectron spectroscopy, scanning electron microscopy, silver-gold alloys, silver-mercury amalgams, corrosion, electrocleaning
Summary for Lay Audience

The research described in this dissertation concerns the analysis of 19\textsuperscript{th} century daguerreotypes. The project had three goals: 1) to gain a deeper understanding of the physics and chemistry of the daguerreotype surface and how the surface degrades with time, 2) to develop alternate methods for preserving the content of these images by refining existing electrocleaning systems, and 3) to make specific recommendations for the preservation and restoration of historically significant daguerreotypes.

The first goal was addressed by using X-ray absorption near edge structure (XANES) spectroscopy to study a freshly prepared reference daguerreotype. The results suggest that inter-diffusion of gold and silver leads to the development of a silver-gold alloy, whose composition varies across the surface and with depth. This was confirmed with laboratory and synchrotron-based X-ray photoelectron spectroscopy. Subsequently, 19\textsuperscript{th} century daguerreotypes were examined with XANES spectroscopy and X-ray fluorescence (XRF) microscopy. This provided information on the elemental distribution and speciation of tarnish on the daguerreotype surface. Finally, completely obscured daguerreotypes, were retrieved with rapid scanning, synchrotron-based micro-XRF imaging. Importantly, this rapid scanning imaging provides curators with an image recovery method for degraded daguerreotypes, even if the artifact’s condition is beyond traditional conservation treatments, and fulfills part of the second goal of this thesis.

The second goal was fully accomplished when a more effective electrocleaning system was developed and produced in collaboration with John McElhone at the National Gallery of Canada (NGC). This enhanced system and was subsequently used to treat 19\textsuperscript{th} century daguerreotypes with two different electrocleaning methods: the original method proposed by Barger (1982) and a second put forward by Wei (2011). Micro-XRF, at both specific regions and across the entire plates, revealed that when used correctly, both processes significantly reduced the sulfur and chlorine surface contamination without dulling the surface. However, both electrochemical methods used in this study resulted in a loss of mercury and gold from the surface.
Specific recommendations for the preservation and conservation of these historical photographs (Goal 3) are discussed throughout and in the conclusions chapter of this thesis.
Co-Authorship Statement

This thesis contains materials from previously published manuscripts. Dr. Tsun-Kong Sham, Dr. Ronald R. Martin, and Dr. Andrew J. Nelson are co-authored on all published papers. Dr. Ian Coulthard is co-authored on the majority of the published papers and played a key role in coordinating synchrotron beamtime. They all played a major role in editing and revising the content presented within this thesis. In collaboration with this committee I devised and conducted the experiments, analyzed the data, wrote the first draft of each manuscript, and guided each text through the submission and revision process.

The daguerreotypes analyzed in this thesis were kindly provided in partnership with John McElhone at the Canadian Photography Institute at the National Gallery of Canada, Ottawa, Canada. Dr. Michael Robinson of Century Dark Room, Toronto, Canada, kindly supplied the test daguerreotypes discussed in Chapter 3 and provided insights and expertise throughout the course of my graduate work. Both individuals also served as co-authors in portions of the work presented in this thesis.

Technical support with synchrotron spectroscopy measurements at the Canadian Light Source (CLS) were provided by the following people: Yongfeng Hu, Qungfeng Xiao, and Aimee Maclennan for measurements performed at the SXRMB beamline, and Dr. Jun Li for measurements performed at the VESPERS and HXMA beamlines. This work is presented in Chapters 3 (SXRMB, VESPERS, and HXMA), 4 (SXRMB), and 6 (SXRMB). Measurements collected at the Cornell High Energy Synchrotron Source (CHESS), which are presented in Chapters 5 and 6, were performed under the assistance and support of Dr. Arthur Woll and Dr. Louisa Smieska.

Scanning electron microscopy graphs presented throughout were taken with assistance from Todd Simpson at Nanofabrication Laboratory, The University of Western Ontario. X-ray photoelectron spectroscopy measurements in Chapter 2 were performed by Mark Biesinger, Surface Science Western.
To my family
Acknowledgments

Firstly, this work was made possible by the unwavering support, guidance, and encouragement of my supervisors: Dr. Tsun-Kong Sham, Dr. Ronald Martin, Dr. Andrew Nelson, and Dr. Ian Coulthard. Moreover, without the foresight and progressiveness of Dr. Sham, this thesis would not have been achievable. It has been an honor and a privilege to have these four intellectuals, who are all experts in their respective fields, demonstrate to me their insights, critical thinking and enthusiasm in studying science, especially in application to the Cultural Heritage sector. Throughout my graduate studies, I have been encouraged and supported to attend domestic and international conference, to participate in synchrotron experiments at a variety of international research laboratories, and collaborate and foster relationships with individuals at a variety of academic, governmental, and private institutions, providing me with a breadth of versatility that will benefit me for the rest of my career.

Secondly, I want to thank my group members from both past and present: Dr. Yun-Mui Yiu, Dr. Zhiqiang Wang, Dr. Xiaoxuan Guo, Dr. Mohammad Norouzi Banis, Dr. Olga Lobacheva, Dr. Stephen Naftel, Dr. Jun Li, Dr. Biwei Xiao, Dr. Biqiong Wang, Dr. Wei Xiao, Mr. Jiatang Chen, Mr. Hendrick Chan, Ms. Yingying Jiang, Mr. Aditya Balaji, Ms. Minsi Li, Ms. Fei Sun, Mr. Jiwei Wang, Mr. Yipeng Sun, and Ms. Xuejie Gao, for all of their valuable suggestions and constructive feedback.

I also want to thank the technical supporters: Dr. Tom Regier, Dr. Jian Wang, Dr. Yongfeng Hu, Dr. Qunfeng Xiao and Dr. Ning Chen from the Canadian Light Source; Dr. Yifan Ye, Dr. Yuchen Shao and Dr. Yisheng Liu from the Advanced Light Source; Mr. Todd Simpson and Mr. Tim Goldhawk from Nanofabrication Laboratory, and Dr. Richard Gardiner from Biotron at the University of Western Ontario (UWO).

Moreover, I would like to thank my collaborators, Mr. John McElhone and Mr. Stephen Gritt at the National Gallery of Canada (Ottawa, Canada) for supplying the daguerreotypes used throughout this study. Their enthusiasm and support facilitated opportunities I would not have thought possible. I will always cherish the collaborative trust that was established during my graduate studies.
Research at the University of Western Ontario (UWO) is supported by the Discovery Grant of the Natural Science and Engineering Research Council of Canada (NSERC), the Canada Research Chair (CRC) Program, the Canada Foundation for Innovation (CFI), and the Interdisciplinary Initiative (IDI) grant of UWO. Canadian Light Source (CLS) is supported by CFI, NSERC, National Research Council (NRC), Canadian Institute for Health Research (CIHR), and the University of Saskatchewan. I acknowledge the receipt of support from the CLS Graduate Student Travel Support Program from 2014 to 2018, and I gratefully acknowledge the Nanofabrication Facility at the University of Western Ontario for SEM imaging and EDX mapping. Advanced Photon Source, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science by Argonne National Laboratory, is supported by the U.S. DOE under Contract No. DE-AC02-06CH11357.

My love for the arts and the sciences grew, as I did, from the support, education, and curiosity provided by my parents, Donna and Larry Kozachuk. My mother, a professional musician, and my father, a welder, instilled in me an interdisciplinary and growth mindset that propelled my education. Without them, and my brother, Paul Kozachuk, the completion of this degree would not have been possible. Much adoration and gratitude goes to my partner, Justin Spencer, who has provided unconditional love and support throughout my pursuit of a Ph.D. in Chemistry. He has pushed me to be a better scientist, critical thinker, and person. Thank you for always being in my corner.
# Table of Contents

Abstract......................................................................................................................................... i

Summary for Lay Audience............................................................................................................. iii

Co-Authorship Statement ................................................................................................................ v

Acknowledgments.......................................................................................................................... vii

Table of Contents ........................................................................................................................... ix

List of Tables ................................................................. xiii

List of Figures ................................................................................................................................. xiv

List of Appendices ......................................................... xviii

List of Abbreviations ....................................................................................................................... xix

Chapter 1 ................................................................................................................................. 1

1 Introduction .............................................................................................................................. 1

1.1 Conservation Science, an Overview ........................................................................... 1

1.2 The Daguerreotype Process .................................................................................. 3

1.3 Daguerreotype Deterioration .............................................................................. 5

1.4 History of Daguerreotype Conservation ................................................................ 8

1.5 Synchrotron Radiation ....................................................................................... 10

1.6 Synchrotron Radiation in Application to Cultural Heritage ......................... 15

1.7 Thesis Outline ........................................................................................................ 16

1.8 References ............................................................................................................. 18

Chapter 2 ............................................................................................................................ 27

2 Experimental Techniques ....................................................................................................... 27

2.1 Synchrotron Radiation Sources .......................................................................... 27

2.1.1 Canadian Light Source ............................................................................ 27

2.1.2 Cornell High Energy Synchrotron Source ........................................... 31
2.2 Synchrotron Techniques .......................................................................................... 33
  2.2.1 X-ray Absorption Spectroscopy ........................................................................ 33
  2.2.2 De-excitation Process ...................................................................................... 38
  2.2.3 X-Ray Fluorescence Imaging ........................................................................... 40
  2.2.4 X-ray Photoelectron Spectroscopy ................................................................ 41
2.3 Scanning Electron Microscopy ............................................................................ 43
2.4 Electrocleaning ..................................................................................................... 44
2.5 References ............................................................................................................ 45
Chapter 3 .................................................................................................................. 49
  3 The Application of XANES and XPS to the Daguerreotype Surface .................... 49
  3.1 Introduction ......................................................................................................... 49
  3.2 Materials and Methods ...................................................................................... 50
    3.2.1 Sample Selection and Preparation ............................................................... 50
    3.2.2 X-ray Absorption Near Edge Structure ......................................................... 51
    3.2.3 Data Processing ............................................................................................. 53
    3.2.4 X-ray Photoelectron Spectroscopy ............................................................... 54
    3.2.5 Scanning Electron Microscopy ..................................................................... 55
  3.3 Results and Discussion ....................................................................................... 56
    3.3.1 Ag L₃-edge XANES ...................................................................................... 56
    3.3.2 Au L₃-edge XANES ...................................................................................... 58
    3.3.3 Hg L₃-edge XANES ...................................................................................... 62
    3.3.4 S K-edge XANES .......................................................................................... 63
  3.4 XPS Analysis ...................................................................................................... 64
    3.4.1 Laboratory-Based XPS Results ..................................................................... 64
    3.4.2 Synchrotron-Based XPS Results ................................................................. 69
  3.5 Conclusions ......................................................................................................... 72
# 3.6 References

Chapter 4

# 4 Analysis of 19\textsuperscript{th} Century Daguerreotypes with Synchrotron Light: a XRF and \(\mu\)-XANES Analysis

## 4.1 Introduction

## 4.2 Materials and Methods

### 4.2.1 Sample Selection and Preparation

### 4.2.2 X-ray Absorption Near Edge Structure

### 4.2.3 X-ray Fluorescence

### 4.2.4 Synchrotron Data Processing

### 4.2.5 Scanning Electron Microscopy Energy Dispersive X-ray

### 4.2.6 Optical Microscopy

## 4.3 Results and Discussion

### 4.3.1 Surface Morphology of the Daguerreotype Surface

### 4.3.2 Synchrotron XRF and \(\mu\)-XANES Analysis

## 4.4 Conclusions

## 4.5 References

Chapter 5

# 5 Recovery of Degraded-Beyond-Recognition 19\textsuperscript{th} Century Daguerreotypes with Rapid High Dynamic Range Elemental XRF Imaging

## 5.1 Introduction

## 5.2 Materials and Methods

### 5.2.1 Sample Selection and Preparation

### 5.2.2 Preliminary Conservation Treatments

### 5.2.3 Synchrotron Radiation Analysis

## 5.3 Results and Discussion

### 5.3.1 Optical Examination
5.3.2 Rapid Scanning XRF .................................................. 115
5.4 Conclusions................................................................. 126
5.5 References.................................................................. 127

Chapter 6 ........................................................................ 129

6 Re-Imaging 19th Century Daguerreotypes: a Soft X-ray XRF and Hard X-ray Rapid Scanning XRF Study ...................................................... 129
6.1 Introduction.................................................................. 129
6.2 Materials and Methods ............................................... 130
   6.2.1 Sample Selection and Preparation ......................... 130
   6.2.2 Electrocleaning ...................................................... 131
   6.2.3 Synchrotron Radiation Analysis ............................. 132
6.3 Results and Discussions ............................................. 135
   6.3.1 The Barger Process .............................................. 135
6.4 Conclusions................................................................. 156
6.5 References.................................................................. 157

Chapter 7 ........................................................................ 160

7 Summary and Future Work ........................................... 160
7.1 Conclusions................................................................. 160
7.2 Future Work............................................................... 163
7.3 References.................................................................. 164
List of Tables

Table 2-1 Summary of CLS beamline facilities included in this thesis................................. 27
Table 2-2 Summary of CHESS beamline facilities included in this thesis........................... 32
Table 3-1 List of beamlines used for each element of interest............................................. 52
Table 3-2 Series of silver-gold alloy standards.................................................................... 53
Table 3-3 Maximum atomic percent and the associated depth................................................. 65
Table 3-4 Binding energies for Hg 4f\(_{7/2}\) and 4f\(_{5/2}\) alongside proposed Hg sources. .......... 68
Table 3-5 Ratio of Au 4f\(_{7/2}\)/Ag 3d\(_{5/2}\)............................................................................... 70
Table 4-1 List of standards used for XANES analysis............................................................. 81
Table 4-2 Scanning parameters for the daguerreotype SR-XRF maps.................................. 82
Table 6-1 Summary of electrocleaning parameters............................................................... 132
Table 6-2 X-ray absorption collection parameters for Ag, S, and Cl.................................... 133
Table 6-3 List of standards used for X-ray absorption near edge analysis.............................. 134
Table 6-4 Average and standard deviation values for Au(L)/Cu(K) ratios.............................. 141
Table 6-5 Average and standard deviation values for Hg(L)/Cu(K) ratios............................. 142
Table 6-6 Average and standard deviation values for Au(L)/Cu(K) ratios............................. 152
Table 6-7 Average and standard deviation values for Hg(L)/Cu(K) ratios............................. 153
List of Figures

Figure 1-1 An optical image of daguerreotype ................................................................. 4

Figure 1-2 (Left) optical image of daguerreotype ............................................................. 5

Figure 1-3 Pourbaix diagram for an Ag-S-Cl-CO$_2$-H$_2$O system ........................................ 7

Figure 1-1 Schematic layout of synchrotron radiation facility [48]. ................................ 11

Figure 1-2 (A) Spatial and (B) spectral distributions of bending magnets, ......................... 13

Figure 1-3 An illustration of the resulting reflection and/or diffraction ............................... 13

Figure 1-4 A schematic representation of (A) a double-crystal monochromator and (B) Bragg diffraction .......................................................................................................................... 14

Figure 2-1 Schematic layout of the CLS Experimental Hall as of January 2019 [1]. .......... 28

Figure 2-2 Layout of SXRMB beamline at CLS [2] ............................................................. 29

Figure 2-3 Layout of HXMA beamline at CLS [4] ............................................................. 30

Figure 2-4 Layout of VESPERS beamline at the CLS [6] .................................................. 31

Figure 2-5 Log-log plot of X-ray absorption cross section ($\sigma$) of mercury ..................... 34

Figure 2-6 Example of a normalized absorption spectrum .................................................. 35

Figure 2-7 Schematic of the outgoing photoelectron wave ................................................. 37

Figure 2-8 Schematic of the multiple scattering process ...................................................... 38

Figure 2-9 Illustration of the de-excitation processes ......................................................... 39

Figure 2-10 Schematic of a single/photon ejection process .................................................. 42

Figure 2-11 Universal curve for the inelastic mean free path as a function of kinetic energy for synchrotron radiation [23] .......................................................... 43
Figure 3-1 Optical images of (A) full daguerreotype test plate and (B) close up of examined area with labelled regions of interest. ................................................................. 50

Figure 3-2 Optical images of daguerreotype test plates................................................................. 55

Figure 3-3 Ag L$_3$-edge XANES for test plate................................................................. 56

Figure 3-4 Comparison of (A) the Ag L$_3$-edge alloy standards and (B) amplification of near edge region for daguerreotype regions. ................................................................. 57

Figure 3-5 Au L$_3$-edge XANES from daguerreotype test plate................................. 59

Figure 3-6 Au L$_3$-edge. ........................................................................................................... 61

Figure 3-7 Hg L$_3$-edge from daguerreotype test plate................................................................. 63

Figure 3-8 Sulfur K-edge of daguerreotype plate......................................................................... 64

Figure 3-9 XPS spectra of L1 (bright region) to a depth of (A) 45 nm and (B) 20 nm........ 65

Figure 3-10 Depth scans for Ag, Au, Hg, I, Cl, O, and S at all regions studied (L1 - bright, L2 - medium, L3 - dark). .............................................................................................................. 66

Figure 3-11 Laboratory-based XPS Hg fine scans and SEM images collected from the daguerreotype test from area (A) L1: bright; (B) L2: medium; and (C) L3: dark. ............... 67

Figure 3-12 Comparison of region S2 (dark) at 3.0 keV (surface) and 8.0 keV (bulk)......... 69

Figure 3-13 HE-XPS VB collected at 3.0 keV from the daguerreotype test ......................... 71

Figure 4-1 Daguerreotypes of an (A) unidentified woman (accession number SC1) (B) and an unidentified man and woman................................................................. 79

Figure 4-2 SEM images from daguerreotype SC1................................................................. 84

Figure 4-3 Optical microscope images showing the variety of tarnish features found on the surface of SC1 (Figure 4-1A). .............................................................................................................. 85

Figure 4-4 SEM electron image from plate SC1 ......................................................................... 86
Figure 4-5 SEM electron image of the woman’s eye on daguerreotype PSC 70:112. .......... 87
Figure 4-6 SEM images from PSC 70:112 ........................................................................................................ 87
Figure 4-7 SEM-EDX Kα line images for Cu, C, S, Cl, and O from tarnished surface of
daguerreotype PSC70:112 ............................................................................................................................... 88
Figure 4-8 SR-based XRF and µ-XANES collected from a blemish observed on the SC1... 89
Figure 4-9 SR-based XRF and µ-XANES collected from a bubble observed on daguerreotype
SC1.................................................................................................................................................................. 91
Figure 4-10 SR-based XRF and µ-XANES from a tarnished spot on daguerreotype SC1. ... 93
Figure 4-11 SR XRF maps from daguerreotype PSC70:112................................................. 95
Figure 4-12 SR XRF maps for Ag, Cl, and S from plate SC1................................................. 98
Figure 4-13 Ag L3-edge ............................................................................................................................... 100
Figure 5-1 Optical images of 19th century daguerreotype ...................................................... 111
Figure 5-2 Micro-XRF spectrum for daguerreotype PSC70:111. ........................................... 114
Figure 5-3 (A) An example of spectral decomposition from the XRF spectrum of a 19th
century daguerreotype from the National Gallery of Canada..................................................... 114
Figure 5-4 (A) Optical image of plate SC1......................................................................................... 117
Figure 5-5 (A) An optical image of plate PSC 70:111.. ................................................................. 118
Figure 5-6 Micro-X-ray fluorescence image of Hg (Lα1,2) from plate PSC 70:111. ......... 119
Figure 5-7 Micro-X-ray fluorescence (µ-XRF) image of Hg (Lα1,2) of plate SC1............ 121
Figure 5-8 Spectral decomposition from the XRF spectrum of plate PSC 70:111............ 124
Figure 5-9 One-dimensional scan on the linear scale of Hg L fluorescence across the jacket
lapel, vest, and white collared shirt of daguerreotype PSC 70:111................................................. 125
Figure 6-1 Images of 19th century daguerreotypes before (1) and after (2) electrocleaning. 130
Figure 6-2 Before (top) and after (bottom) Barger electrocleaning data for PSC 70:112. ... 137
Figure 6-3 Before and after Barger electrocleaning data (PSC 70:112).............................. 138
Figure 6-4 Before and after Barger electrocleaning data (PSC 70:112).............................. 140
Figure 6-5 Micro-XRF images from before (top) and after (bottom) Wei cleaning for RCLSC1.............................................................. 144
Figure 6-6 Before and after Wei electrocleaning data from RCLSC1............................... 146
Figure 6-7 Before and after Wei electrocleaning data from RCLSC1............................... 147
Figure 6-8 Before (top) and after (bottom) Wei electrocleaning μ-XRF images for SC1... 149
Figure 6-9 Before and after Wei electrocleaning data from SC1 ................................. 150
Figure 6-10 Before and after Wei electrocleaning data from SC1 ............................... 151
Figure 6-11 Regions of interest for Au(L)/Cu(K) and Hg(L)/Cu(K) values from SC1 from both the left and right side of the plate. ................................................................. 154
List of Appendices

Appendix A: Copyright Release from NRC Research Press .................................................. 165

Appendix B: Copyright Release from Alexandru Ioan Cuza University Publishing House 166

Appendix C: Copyright Release from Nature Publishing Group ........................................ 167

Appendix D: Copyright Release from Springer Publishing ................................................ 168

Appendix E: Copyright Release from IUCr ................................................................. 169

Appendix F: Linear Combination Fit Results for all Relevant Absorption Spectra ............. 170
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>BE</td>
<td>Binding energy</td>
</tr>
<tr>
<td>BM</td>
<td>Bending magnet</td>
</tr>
<tr>
<td>CHESS</td>
<td>Cornell High Energy Synchrotron Source</td>
</tr>
<tr>
<td>CLS</td>
<td>Canadian Light Source</td>
</tr>
<tr>
<td>CPI</td>
<td>Canadian Photography Institute</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy dispersive X-ray</td>
</tr>
<tr>
<td>EXAFS</td>
<td>Extended X-ray absorption fine structure</td>
</tr>
<tr>
<td>FLY</td>
<td>Fluorescence yield</td>
</tr>
<tr>
<td>HXMA</td>
<td>Hard X-ray MicroAnalysis</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>KE</td>
<td>Kinetic energy</td>
</tr>
<tr>
<td>LCF</td>
<td>Linear combination fitting</td>
</tr>
<tr>
<td>LINAC</td>
<td>Linear accelerator</td>
</tr>
<tr>
<td>(\mu)-XANES</td>
<td>micro-X-ray absorption near edge structure</td>
</tr>
<tr>
<td>(\mu)-XRF</td>
<td>micro-X-ray fluorescence</td>
</tr>
<tr>
<td>(\mu)-XRD</td>
<td>micro-X-ray diffraction</td>
</tr>
<tr>
<td>NGC</td>
<td>National Gallery of Canada</td>
</tr>
<tr>
<td>PFY</td>
<td>Partial fluorescence yield</td>
</tr>
<tr>
<td>RF</td>
<td>Radio frequency</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>ROI</td>
<td>Region of interest</td>
</tr>
<tr>
<td>SCE</td>
<td>Standard calomel electrode</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>SR</td>
<td>Synchrotron radiation</td>
</tr>
<tr>
<td>SXRMB</td>
<td>Soft X-ray Microcharacterization Beamline</td>
</tr>
<tr>
<td>TEY</td>
<td>Total electron yield</td>
</tr>
<tr>
<td>UWO</td>
<td>University of Western Ontario</td>
</tr>
<tr>
<td>VESPERS</td>
<td>Very sensitive Elemental and Structural Probe Employing Radiation from a Synchrotron</td>
</tr>
<tr>
<td>WL</td>
<td>Whiteline</td>
</tr>
<tr>
<td>XAFS</td>
<td>X-ray absorption fine structure</td>
</tr>
<tr>
<td>XANES</td>
<td>X-ray absorption near edge structure</td>
</tr>
<tr>
<td>XAS</td>
<td>X-ray absorption spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
</tbody>
</table>
Chapter 1

There are two kinds of truth: the truth that lights the way and the truth that warms the heart. The first of these is science, and the second is art. Neither is independent of the other or more important than the other. Without art, science would be as useless as a pair of high forceps in the hands of a plumber. Without science, art would become a crude mess of folklore and emotional quackery. The truth of art keeps science from becoming inhuman, and the truth of science keeps art from becoming ridiculous.

Raymond Thornton Chandler, writer (1888 – 1959)

1 Introduction

1.1 Conservation Science, an Overview

Conservation science is an established and active area of scientific research, that consists of the application of scientific principles to further the chemical and physical understanding of objects of cultural significance in order to better conserve them [1]. This interdisciplinary field engages a diverse range of scholars, museum professionals, and technicians from disciplines including art history, art conservation, chemistry, biology, physics, archaeology, ethnography, and museology, to name a few.

Throughout history, the application of science and technology to the preservation and restoration of objects has propelled and advanced ancient societies and cultures. From the non-destructive testing technique Archimedes used to determine the composition of gold alloys [2] to the reading of Herculaneum papyri with X-ray fluorescence spectroscopy and computed tomography [3], the objective of conservation science has been to further understand the chemical and physical composition of ancient objects, which is then applied to an object’s repair and/or stabilization.

The 18th century saw the first published work on a conservation study, the analysis of Greek and Roman coins by Martin Heinrich Klaproth [4], and in the 19th century, a
handful of fine art institutions created dedicated conservation departments, whose initial task was to investigate the degradation of paintings [5]. Between 1925 and 1975, the field of conservation science in the United States experienced a surge of innovative advancement and growth [5]: museums and educational institutions continued to add conservation departments and analytical laboratories, conservation science journals were published, and training programs and professional societies were founded. Moreover, the hiring of chemists and the pursuit of technical investigations by artistic institutions was encouraged.

Since 1975, institutions have continued to expand their conservation science divisions and there has been an increased awareness of the importance for minimally invasive techniques. Moreover, given the perpetual technological advancements observed in the 21st century, there is an increasing need for collaboration between scientific institutions with museums and art historical organizations to ensure these scientific innovations are applied to objects of cultural significance [6]. The National Science Foundation has issued reports acknowledging cultural heritage, and its preservation and scientific examination, to be a major economic resource with respect to tourism [6,7].

Presently, conservation is defined as the documentation, analysis, cleaning, and stabilization of an object [8]. The preservation of an object involves maintaining it in its existing condition, minimizing the rate of change, and attempting to slow down further deterioration and/or prevention of damage. Restoration refers to the repair of damaged objects and the replacement of missing parts [8]. Conservation science plays a crucial role throughout an object’s treatment. It can provide insights beyond simple visual analysis, revealing information such as the chemical composition of the object or its degradation products and how they vary across the surface and with depth. Moreover, conservation science can be used in determining the provenance and/or age of an object, for authenticity verification, and to establish which conservation techniques should be used during subsequent conservation and restoration [9].

While most conservators prefer non-invasive or minimally invasive methods, conservation science can use both destructive and non-destructive analytical methods.
The kind of technique used depends on, but is not limited to: 1) the research question, 2) the material of the object, 3) how delicate the item in question is, 4) if the object can be transported or, if it is too fragile to move, 5) if a sample can be collected from it, and 6) how heterogeneous the artifact is. Heterogeneity is a common feature of cultural heritage materials and often poses a challenge to conservationists and conservation scientists alike. This heterogeneity can arise from the object’s production process, aging and environmental exposure, and/or previous conservation efforts [10]. When selecting instrumentation, multiple factors should be considered. The technique utilized needs to be 1) precise and reproducible, 2) highly sensitive, 3) versatile (i.e., should be able to concurrently detect multiple elements), and 4) highly accurate. While not always possible, non-destructive, non-invasive, and non-contact techniques are extremely valuable for conservation science studies. One such technique that has successfully applied to the field of cultural heritage is synchrotron radiation.

1.2 The Daguerreotype Process

Louis-Jacques-Mandé Daguerre (1787-1851) invented the daguerreotype in 1839 (Figure 1-1). It was popular in Europe and North America between 1839 and 1860 [11-14]. Unlike the predominantly uniform methodology of today’s photographic process, chemical individuality is a distinctive feature to the daguerreotype. They are one-of-a-kind images with no associated negatives that represent the first opportunity to permanently and realistically document our world. Daguerre’s original method took a highly polished, silver coated copper plate and exposed it to iodine vapour to produce a light sensitive surface. Subjecting the plate to light superimposed the scene (in mirror image) on the surface of the plate through the formation of silver particles [15]. This development of image particles corresponded with the intensity of light in the scene: regions of high light intensity produced regions of image particles with relatively uniform size, shape, and density (defined as the number of particles per unit area) and regions that had minimal light exposure created image particles that were inconsistent in size, shape, and distribution [16]. The image particles in high density and midtone regions have been reported to have diameters of 0.1 – 1 µm and 0.25 – 2.5 µm, respectively. An example of a high density image particle region would be the white collar of the woman’s dress in
Figure 1-2. In contrast, shadow/dark tone parts (such as the tree in the background of the image in Figure 1-2) contain particles ranging from 10 – 50 µm [16] although particles with a diameter less than 10 µm are often observed. These spatial and size variations of image particles create the vast range of gray tones that are characteristic of daguerreotypes [14].

After the production of this latent image, the image is fixed by exposure to heated mercury vapour, which produces a silver-mercury amalgam. Unreacted silver halides were chemically washed off with a thiosulfate solution before a final rinse with water [17-20]. Later modifications to the production process included the addition of different halides, such as chlorine and bromine, along with a gilding step, an electroless deposition of gold onto the plate’s surface. This later process, invented by Armand Hippolyte Louis
Fizeau (1819-1896), improved the brilliance, contrast, and durability of the daguerreotype image [12,21].

Figure 1-2 (Left) optical image of daguerreotype PSC 70:112 with (right) SEM images from a shadow (top right) and highlight (bottom right) region.

1.3 Daguerreotype Deterioration

Despite being placed within a frame and behind cover glass for protection, these metallic plates are prone to corrosion [22-24], often in the form of white (silver chloride (AgCl)), brown/red (copper (I) oxide (Cu$_2$O)), and/or black films (copper (II) oxide (CuO), copper sulfide (CuS), silver sulfide (Ag$_2$S), silver sulfate (Ag$_2$SO$_4$), and silver oxide (Ag$_2$O)), which distort and can sometimes completely obscure the photographic image [25,26]. Silver and copper cyanide products have also been observed on the daguerreotype surface, a result of previous conservation efforts [27].

The causes for daguerreotype image degradation could include a variety of factors including pre- and post-production conditions, such as their storage and display settings,
any past treatments, exposure to atmospheric pollutants, variation in temperature and humidity, daguerreotype case integrity (i.e., whether or not the original package seal was broken), and the materials used in the production of the plate, glass, and case. It is often the case that little is known regarding the history of production and care of these objects, which further complicates preservation and conservation efforts.

Barger and White [26] noted that Ag₂S and AgCl are the two most common degradation products observed on the daguerreotype surface. Silver oxide is also often noted. In general, these compounds are the result of exposure to H₂S (0.3 ppb), HCl (0.4 ppb), and O₂ (2.1 × 10⁸ ppb) [26]. The concentrations of other compounds that may adsorb into the electrolyte layer and instigate corrosion have been reported as COS (0.6 ppb), SO₂ (30 ppb), and Cl₂ (not detected) [28-31].

Silver corrosion films characteristically form and proliferate in a non-uniform manner, often forming dendrites and whiskers, which have been observed in controlled and uncontrolled laboratory studies [32-35]. This inhomogeneity may be a result of surface moisture being locally collected, thereby producing non-uniform corrosion initiation or nucleation regions. A variety of factors impact the rate of corrosion, such as mixed gaseous environments, the concentration of the environmental contaminants, temperature, and humidity [36].

Figure 1-3 shows the Pourbaix diagram for Ag in a system with S, Cl, CO, and H₂O [26]. Pourbaix diagrams show regions of stability for metals, their ions and corrosion products as a function of the potential and of the pH of the aqueous system, thereby providing theoretical thermodynamic information of how a given metal reacts within an aqueous environment. Solid lines in Pourbaix diagrams indicate that the two species on either side of the line are in equilibrium while dashed lines indicate areas in which water is stable. The most stable specie is indicated within each region, such as the two most common degradation compounds observed on daguerreotypes, Ag₂S and AgCl. Specifically, Figure 1-3 shows that Ag₂S is stable in typical conditions for water in atmospheric conditions (i.e., neutral and acidic pH solutions at a few tenths of a volt vs. saturated
calomel electrode (SCE)). From Figure 1-3, it is apparent that under several different conditions, Ag is stable and mostly corrosion resistant.

Figure 1-3 Pourbaix diagram for an Ag-S-Cl-CO₂-H₂O system at 25 °C, with a sulfur activity of 0.1 M, chlorine activity of 0.05 M, carbon concentration of 0.01 M, and dissolved silver concentration of 1 µM. A saturated calomel electrode (SCE) was used as the reference. Defined regions indicate areas of compound stability at a given pH and potential. Water is stable within the dashed line regions [26].

When oxygen and water vapour are both present, the formation of Ag₂S on the surface can occur either through direct sulfidation or in the presence of adsorbed oxygen [56]. This process can arise from either the reduction of H₂S to HS⁻ ions in the electrolyte layer, which then go on to form Ag₂S [26], or from COS that is hydrolyzed to H₂S upon reacting with the moisture on the silver surface [25]. As the formation of Ag₂SO₄ has
only been shown to occur when the concentration of SO$_2$ (g) are two to three times greater than atmospheric conditions, this particular corrosion process has a minimal impact on the corrosion of the silver surface [24,36].

Residual silver halides may be present on the plate from either the sensitizing step or from the gilding step (as a gold-chloride-sodium thiosulfate solution was used), and/or from environmental contamination [21]. The production of Ag$_2$O on the surface of daguerreotypes is speculative; it may arise from ozone trapped in the case or from the formation of a highly basic environment, perhaps due to cover glass deterioration (see the Pourbaix diagram in Figure 1-3).

The deterioration of the cover glass used to protect the daguerreotypes from chemical and/or atmospheric conditions, dust and debris, or from mechanical damage, may also induce surface corrosion. For example, Barger [37] suggested that deterioration of the cover glass as well as the geometry and composition of the frame might lead to deterioration of daguerreotypes. Patchy areas of discolouration, distinct clusters of amber coloured “crystals”, cloudiness, and sticky droplets (termed “weeping” glass) are just a few features observed on 19$^{th}$ century cover glasses [37]. Cover glass decomposition has been suggested to lead to the deposition of Na$_2$SO$_4$, BaSO$_4$, NH$_4$Br, Ag, AgCl, Ag$_3$PO$_4$, HCOONa, and Cu$_2$O. Such deterioration is the result of alkali ions in the glass network reacting with water vapour and other airborne gasses [37]. For example, one route of 19$^{th}$ century glass corrosion involves the migration of Na$^+$ and K$^+$ to the surface through an ion-exchange reaction with hydrogen ions, a reaction that is dependent on the moisture content of the atmosphere [38,39]. Apart from daguerreotypes, glass deterioration is of concern to conservation scientists working within the cultural heritage sector on stained glass objects and glass beads [19,38,39].

1.4 History of Daguerreotype Conservation

The conservation of daguerreotypes has been a long-standing topic of discussion and, at times, has been a point of contention [22,27]. The goal of a cleaning treatment for a daguerreotype is to preserve the optical integrity of the image while removing the tarnish from the surface (i.e., particle density and shape is unchanged and the surface retains its
A treatment process that is controllable and somewhat forgiving is highly desirable [27]. Given the inherent individuality of each daguerreotype and their variable chemistry, which depends on, but is not limited to, their production, how they have been stored and handled, and any past conservation efforts, the determination of the correct treatment for daguerreotypes is a challenge and some treatment methods have caused the fading and/or complete loss of historic images.

Historically, if abrasive procedures could not be used to remove Ag$_2$S and/or Ag$_2$O, immersing an object in a silver dip cleaner, such as potassium or sodium cyanide and/or acidic thiourea solutions, was deemed appropriate. It was observed that when this technique was applied to daguerreotypes however, the lack of control and selectivity, resulted in surface etching that degraded a plate’s optical properties, the formation of “measles” on the surface (for thiourea cleaning specifically), and the development of silver cyanide and silver-thiourea complexes, which are extremely detrimental to the daguerreotype surface [27]. Other methods for daguerreotype treatments that have been explored have included sputter cleaning [22], the application of excimer lasers [40], and atmospheric pressure non-equilibrium plasma [41]. Generally, in the museum setting, rinsing with an ammonium solution [14,42] and the replacement of the cover glass [27] are the only procedures performed.

The electrocleaning process, which was originally proposed by Barger et al. [16,27], applied an external current with a movable aluminum electrode (counter electrode) over the daguerreotype (working electrode), which was placed in an electrolyte bath (NH$_4$OH; pH = 12). A platinum wand was later introduced, as it was observed that the more noble the counter electrode, the better the cleaning results. Altering the potential of the daguerreotype between anode and cathode in repeated cycles resulted in the substantial removal of surface tarnish. The plate was then rinsed and dried. Da Silva et al. [17] have demonstrated success with a modified electrocleaning method where they alternated between a basic (1% w/v sodium metaborate) and an acidic (0.3% w/v citric acid) solution while varying the potential to alternate the daguerreotype from the system anode to being the cathode. While both the Barger and Da Silva method improved the appearance of the daguerreotype and did not appear to negatively impact the surface,
concerns regarding the removal of silver due to the alternating current have been expressed, specifically with the Barger method. An alternative method suggested by Wei et al. [73] applies only a cathodic potential to avoid the oxidation of silver on the surface. This was conducted in an electrolyte solution of 0.1 M NaNO$_3$ (approximately pH = 6). An in-depth study of the Wei method can be found in reference 74. Throughout the literature, including the Barger and Wei studies, only localized regions of treated plates have been examined pre- and post-electrocleaning, offering a limited view of any variations in chemical or physical morphology.

As in any scientific examination of an object of cultural significance, it is important to understand the inherent chemistry of the daguerreotype, and how the production process can alter the visual, chemical, and physical appearance of the final image. The dissertation recently produced by Dr. Michael Robinson [45] provides a comprehensive discussion and examination on this topic.

The goal of the work presented in this thesis is to contribute to the daguerreotype literature through furthering the chemical and physical understanding of the daguerreotype surface, providing a new imaging method for degraded daguerreotypes as well as highlight that the impact of the electrocleaning method is not negligible. It is the hope that this work aids the conservation community to make more informed decisions when the care of daguerreotypes is concerned.

### 1.5 Synchrotron Radiation

Synchrotron radiation (SR) is the tangential electromagnetic radiation produced by electrons that are accelerated to approximately the speed of light and are steered in a curved orbit by an external magnetic field. Although theoretically predicted in 1873 by Maxwell, who stated that altering charge densities and electric currents would produce radiated, electromagnetic fields, SR was not visually observed until 1947 [46]. Since the inaugural SR facility (i.e., Tantalus I) became operational in 1968 [47], there are currently over 60 operational synchrotron light sources that are accessible to general users. Figure 1-4 presents the typical design of a modern SR facility.
Synchrotron light is produced by heating an electron gun (a metal oxide cathode) to \(\sim 1000\ \degree C\), which then produces electrons that are subsequently injected into a linear accelerator (LINAC). Once in the LINAC, accelerating electrons that approach the speed of light, attain an energy on the order of mega-electronvolts (MeV) under high voltage. By guiding the electrons into a booster ring, the energy is increased to the scale of giga-electronvolts (GeV). In order to maintain the stability of the electron beam within the booster ring, the electrons are circularly directed via dipole magnets or bending magnets (BM), as well as being transversally directed by quadrupole magnets. Any energy loss experienced due to synchrotron radiation is replenished within a radio frequency (RF) cavity (labelled within Figure 1-4) by applying a time-varying electric field, or voltage, within the storage ring, producing a “boost” as it crosses this inserted acceleration device [49]. Finally, the electrons are relocated into a storage ring where they circulate for several hours at close to the speed of light.

Synchrotron technology is classified by generation (zero, first, second, third, and fourth), with the current, third generation, being arguably the most versatile of the technologies. Third generation synchrotrons rely on insertion devices, such as wigglers and undulators, to achieve a much brighter, collimated beam. Wigglers periodically laterally deflect the

Figure 1-4 Schematic layout of synchrotron radiation facility [48].
charged particles that are travelling through the device with short periods of magnets that have a strong magnetic field. This produces a continuum of accelerated electrons with a substantial bend relative to the natural emission angle. Undulators exploit the interference effect that accompanies the shallower bend produced from a longer period, fabricating a more collimated, pseudo-monochromatic beam with a much smaller spatial distribution [49]. Each kind of insertion device generates different spatial distributions and can be distinguished by the opening angle ($1/\gamma$) (equation 1-1).

$$\gamma = \frac{E}{m_0c^2} \approx 1957E \text{ (GeV)}$$

(1-1)

Here, $\gamma$ is the ratio between the mass of a relativistic electron and its rest mass ($m_0$), $E$ is the energy, and $c$ is the speed of light. Figure 1-5 shows how various insertion devices affect the opening angle. The opening angle from wigglers is much larger ($>> 1/\gamma$) than that produced by a BM due to the high magnetic field. Undulators generate a relatively smaller opening angle ($1/\gamma\sqrt{N}$ where $N$ is the number of magnets) due to the application of a less intense magnetic field [50]. Of the two insertion devices, undulators are more commonly used in 3rd generation synchrotron facilities due to their relatively greater brightness (i.e., “usable” radiation), with brightness defined as the number of emitted photons from 1 mm$^2$ of the source per second per solid angle and per 0.1% of bandwidth [51]. If greater intensity over a wide energy range is required however, wigglers are the preferred insertion devices.
Given the inherent capacity of SR to emit a broad range of energies from infrared (IR) to hard X-rays, various optical components can be used to produce an energy-specific photon beam. To direct the beam from the storage ring to the endstation, a collection of slits and mirrors are used and, depending on whether soft (1 – 5 keV) or hard (5 – 40 keV) X-rays are required for the experiment, grating or double-crystal monochromators are used, respectively (Figure 1-6).

Figure 1-6 An illustration of the resulting reflection and/or diffraction from a (A) grating monochromator and (B) Echellette-type grating.
Soft X-rays are produced through the use of grating monochromators, where grating refers to the array of well-defined lines (both in regard to separation and profile). The interaction of the incident beam and the monochromator is based on the theory of diffraction (equation 1-2), where $n$ is the order of the diffraction, $\lambda$ is the wavelength of the diffracting light, $d$ is the distance between the grating lines, and $\alpha$ and $\beta$ are angles of incidence and diffraction, respectively.

$$n\lambda = d(sina \pm sin\beta)$$  \hspace{1cm} (1-2)

When the incident beam reaches the monochromator with a grazing angle, the angles of the diffracted beam depend on the energy of the incident beam. A specific energy can then be selected while maintaining the exit beam at a fixed angle by either rotating the grating or adjusting the optical aperture.

Hard X-rays are monochromatized using a double-crystal monochromator that contain two, identical crystals (i.e., they have the same d-spacing and they are made of the same element). Rotating and translating these two parallel crystals produce an energy-specific beam with a fixed exit angle (Figure 1-7A).

![Figure 1-7 A schematic representation of (A) a double-crystal monochromator and (B) Bragg diffraction.](image)
This process is based on Bragg’s equation (equation 1-3) where \( n \) is the order of diffraction, \( \lambda \) is the wavelength of the photon beam, \( d \) is the lattice spacing (Figure 1-7B), and \( \theta \) is the Bragg angle. Commonly, crystals such as Si(111), Si(333), and InSb(111), which all have different d-spacing, are used for energy selection.

\[
n\lambda = 2dsin\theta
\]  

Overall, compared with traditional X-ray sources, SR has several advantages: 1) Tunability – SR provides continuous or tunable photon energy from infra-red (IR) to gamma rays with BM/wigglers or undulators, respectively; 2) Brightness – SR yields a high flux and highly collimated beam perpendicular to the accelerated direction; 3) Polarization – SR generates linearly polarized photons in the orbit plane and elliptically polarized photons above and below the plane, both tunable with specially designed undulators; 4) Time structure – the RF cavity produces nanosecond to sub-nanosecond pulses of bunched electrons with a micro- or nanosecond repetition rate; and 5) Coherence – SR produced from undulators possess laser-like properties [53].

1.6 Synchrotron Radiation in Application to Cultural Heritage

Synchrotron radiation has assisted in complementing and corroborating a variety of cultural heritage studies. Given the versatility of SR techniques, a wide range of non-destructive, non-contact, non-invasive photon-based spectroscopies [54] and imaging methods [55-57] have been applied to a range of materials including but not limited to cosmetics [58], paints [59,60], paper [61,62], ceramics and pottery [63], glass [64,65], metals [66-68], wooden objects [69,70], and biological remains, such as bone and dentine [51,71,72]. Despite the diverse range of materials that fall under the cultural heritage umbrella, their heterogeneity, limited reproducibility (in regard to sampling statistics), and sample fragility (both physically and chemically) necessitate similar setup requirements when conducting synchrotron experiments. It is often the case that a variety of complementary analytical techniques are required in order to attain a complete picture of these complex systems.
The application of SR to the study of cultural objects can make a significant contribution to the understanding of these ancient artifacts due to the energy tunability, higher photon flux, higher resolution, and the use of micro-beam techniques [73]. For example, the resolution provided by μ-XRF has enabled the imaging of lost paintings “hidden” under existing works of art through 2D visualization of trace elements [74] and when μ-XRF is combined with μ-XANES, simultaneous characterization of the local chemical environment at specific areas of interest within the 2D map can be accomplished [59].

Whenever scientific analysis is applied to works of cultural significance, the possibility of chemical and physical damage [75] should be addressed and while SR can provide significant insights, the risk of beam damage must be considered. For example, while one of the benefits of SR is its ability to achieve a small spot size, the concentration of photons within a small unit area increases the flux and dose received by the sample. Other factors that could impact the integrity of the examined object are: 1) the frequency of the incident irradiation, 2) the material of the object in question, and/or 3) the length of the beam exposure during the experiment. It is important to consider chemical and/or physical deviation due to SR examination during data analysis as any alterations that may occur during the experiment could impact the interpretation of the results. When taken into consideration and the appropriate precautions are put in place however, SR can provide innovative data without harming the artifact in question.

This thesis discusses the application of SR to 19th century daguerreotypes.

1.7 Thesis Outline

This interdisciplinary analysis of 19th century daguerreotypes has three key objectives. The initial goal is to understand the chemistry of the image, how it is produced and how it degrades over time. The second, related goal is to advance the understanding and methodology of the electrochemical cleaning process, using XRF imaging capabilities, specifically at SR facilities; this will enable safe and consistent cleaning of these tarnished images and provide an alternative method of preserving a daguerreotype image when conservation treatments are not possible or undesirable. The third goal is to develop
preservation and restoration recommendations for cultural heritage professionals who have daguerreotypes in their collections.

Whenever scientific investigation is pursued in the cultural heritage sector, it is crucial to consider the impact of such techniques on the object of interest. To ensure that the application of SR to the daguerreotype surface would not induce any negative alteration, Chapter 3 discusses the application of synchrotron-based XANES and X-ray photoelectron spectroscopy (XPS) and laboratory-based XPS to two test plates. Once SR analysis was determined to be a non-destructive and non-invasive method of analysis, the study was expanded to include 19th century daguerreotypes. These plates, which were supplied by the National Gallery of Canada (NGC) research study collection and the Canadian Photography Institute (CPI) collection, had varying degrees of tarnish on their surfaces.

While previous studies have used artificially tarnished test plates to examine the chemical nature of daguerreotype degradation, the work presented here focuses primarily on historic plates. This choice to focus primarily on 19th century plates was determined by a variety of factors. Firstly, despite offering important and relevant information regarding possible degradation compounds, each daguerreotype is unique, due to the complexity of the production process and the variation in the environmental conditions experienced throughout the plate’s lifetime. Secondly, the literature has provided substantial material regarding the variety of tarnish compositions present on silver surfaces as well as the daguerreotype surface. However, while artificially tarnished plates do provide insight into the common corrosion products observed on silver surfaces, the uniqueness of daguerreotypes suggests that accelerated aging studies may not accurately represent the conditions observed on a 19th century plate.

Chapter 4 discusses the application of SR-based XANES spectroscopy and XRF microscopy to 19th century daguerreotypes, revealing information regarding the speciation and distribution of tarnish on historic plates. This chapter expands on the work presented in Chapter 3 and also contributes to the first goal of this thesis: to further the understanding of the tarnish composition and distribution on the daguerreotype surface.
Chapter 5 discusses the application of SR rapid scanning XRF mapping to daguerreotypes. In an effort to further the understanding of mercury’s role in the daguerreian image, Hg fluorescence mapping was pursued. It was determined that through tracking the Hg L emission, the original image could be digitally recovered, even if an image was completely hidden behind a layer of corrosion. While this work does not physically alter the condition of the plate, it does provide an alternative recovering method as tarnished daguerreotypes could be imaged and used for historical studies. This contributes to the second goal of this thesis.

Chapter 6 investigates the second research question by examining the chemical and physical impact of two different methods: the original method proposed by Barger [27] and a second put forward by Wei [43]. This study used synchrotron-based µ-XRF to map the elemental distribution pre- and post-electrocleaning on 19th century daguerreotypes using both soft and hard incident X-rays. X-ray absorption spectroscopy was used to probe local chemistry before and after cleaning.

Conclusions and possible future work, along with recommendations for conservation and recovery of daguerreotypes, is discussed in Chapter 7.

1.8 References


Chapter 2

Most institutions demand unqualified faith; but the institution of science makes skepticism a virtue.

Robert King Merton, sociologist (1910 – 2003)

2 Experimental Techniques

2.1 Synchrotron Radiation Sources

2.1.1 Canadian Light Source

The Canadian Light Source (CLS), located in Saskatoon, Saskatchewan, is Canada’s only synchrotron facility. With a circumference of 171 m, the CLS has a 2.9 GeV storage ring operating at a current up to 500 mA, a radio frequency of 500 MHz, and an emittance of 18.2 nm rad. A schematic layout of the CLS experimental hall can be seen in Figure 2-1. It includes 12 straights (9 available for insertion devices), 24 bending magnets, and over 40 possible beamlines. To date, 14 beamlines are in operation, which provide photon energy range from far infrared (IR) to hard X-ray [1]. A summary of the CLS beamlines and endstations used in this thesis is provided in Table 2-1.

Table 2-1 Summary of CLS beamline facilities included in this thesis.

<table>
<thead>
<tr>
<th>Endstation and Beamline</th>
<th>Energy Range (eV)</th>
<th>Thesis Work</th>
<th>Chapter</th>
</tr>
</thead>
<tbody>
<tr>
<td>SXRMB at CLS</td>
<td>1700 – 10 000</td>
<td>XANES at the Ag L\textsubscript{3} and S, Cl K-edges; XRF images for Ag, S, and Cl; XPS (survey / fine scans and valence band)</td>
<td>Chapters 3, 4, &amp; 6</td>
</tr>
<tr>
<td>HXMA at CLS</td>
<td>5000 – 40 000</td>
<td>Au L\textsubscript{3}-edge of Au-Ag alloy standards</td>
<td>Chapter 3</td>
</tr>
<tr>
<td>VESPERS at CLS</td>
<td>7000 – 30 000</td>
<td>Au and Hg L\textsubscript{3}-edge</td>
<td>Chapter 3</td>
</tr>
</tbody>
</table>
2.1.1.1 SXRMB (06B1-1)

The Soft X-ray Microcharacterization Beamline (SXRMB; 06B1-1) at the CLS comprises four interchangeable endstations with three capabilities: two stations for the X-ray absorption fine structure (XAFS) capability (both ambient and vacuum capabilities), one for high energy X-ray photoelectron spectroscopy (XPS), and the microprobe endstation (Figure 2-2) [2]. The SXRMB is a medium energy X-ray beamline and uses a bending magnet source to produce an energy range of 1.7 – 10 keV [3]. All endstations operate under similar specifications. Here, when the InSb(111) crystal (energy range: 1.7 – 10 keV) is used, an energy resolution ($\Delta E/E$) of $3.3 \times 10^{-4}$ can be achieved. When the Si(111) crystal (energy range: 2 – 10 keV) is used, an energy resolution of $1.0 \times 10^{-4}$ can be attained. The flux and spot size of these two endstations however, are very different; the XAFS endstation has a flux (at 100 mA) over $1.0 \times 10^{11}$ photons/s in a spot size of $\sim 1$ mm $\times$ 4 mm (vertical $\times$ horizontal), whereas the microprobe endstation has a flux of (at 100 mA) of $1.0 \times 10^{9}$ photons/s with a spot size of $\sim 10$ $\mu$m $\times$ 10 $\mu$m (vertical $\times$ horizontal).
horizontal), which is achieved through Kirkpatrick-Baez (KB) micro-focusing mirrors. The sample stage is housed in a separate chamber downstream and is equipped with a Si(Li) drift detector (SDD) (Bruker), a CCD camera and a 3-axis (X, Y and Z) sample stage. Beam alignment and monitoring is achieved by placing a micro-ion chamber between the KB mirror chamber and the sample chamber. The SDD has a moderate energy resolution of ~ 130 eV, sufficient to separate all the fluorescence X-rays of interest in this analysis.

The four sub-endstations at SXRMB are: 1) the solid state endstation specific for bulk analysis of solid samples under high vacuum (10^{-7} torr); 2) the ambient table endstation, which is designed for bulk analysis of samples under ambient pressure and where liquid and solid state in-situ experiments can be performed; 3) the microprobe endstation that provides a 10 × 10 µm beamspot and is used in elemental and chemical mapping experiments; 4) the high energy XPS endstation (photon energy: 2 – 10 keV) offers depth-profiling photoemission analysis by varying energies, which can provide information on surface and bulk properties of the material.

In this thesis, XANES measurements at the Ag L₃-edge, S K-edge, and Cl K-edge and the XRF images for Ag, S, and Cl in Chapters 3, 4, and 6 were conducted at the microprobe endstation. Chapter 3 also includes high energy XPS analysis that was conducted at this beamline.

![Figure 2-2 Layout of SXRMB beamline at CLS [2].](image)

### 2.1.1.2 HXMA Beamline (06ID-1)

With an energy range of 5 – 40 keV, the multipurpose hard X-ray microanalysis (HXMA) beamline (06ID-1) has both XAFS and X-ray diffraction (XRD) endstations (Figure 2-3) [4]. Sourced from a 63 pole superconducting wiggler, the HXMA beamline
can achieve a spot size of 0.8 mm × 1.5 mm (horizontal × vertical), a wavelength of 2.5 – 0.3 Å, an energy resolution (ΔE/E) of 1.0 × 10⁻⁴, and a flux (at 100 mA) of 1.0 × 10¹² photons/s at 12 keV. While XANES and extended X-ray absorption fine structure (EXAFS) are the two primary techniques used with the XAFS endstation at the HXMA beamline, a variety of diffraction experiments are available at the X-ray diffraction (XRD) endstation including but not limited to high pressure powder XRD with a diamond anvil cell, resonance XRD and polarization analysis, and grazing incidence small angle X-ray scattering. The Au L₃-edge of the Au-Ag alloy standards was collected at the HXMA beamline. These results are presented and discussed in Chapter 3.

Figure 2-3 Layout of HXMA beamline at CLS [4].

2.1.1.3 VESPERS Beamline (07B2-1)

The Very sensitive Elemental and Structural Probe Employing Radiation from a Synchrotron (VESPERs) beamline (07B2-1) is a hard X-ray microprobe beamline that uses a bending magnet source (Figure 2-4) [6]. Having a photon energy range of 7 – 30 keV, VESPERS is dedicated to the micro-X-ray diffraction (μ-XRD), specifically Laue diffraction, and micro-X-ray fluorescence (μ-XRF) analysis of materials such as metals and minerals [7]. VESPERS is designed to have its two-branches operate independently while sharing one monochromator; one branch passes through a double crystal monochromator in which two multilayer stacks and a Si(111) substrate are capable of providing several different bandwidth energy windows of 0.01%, 1.5% and 10% while the other optical pathway does not pass through the monochromator, thus producing polychromatic (white) radiation. The general beamline conditions are: 1) an energy
resolution ($\Delta E/E$) of $1.0 \times 10^{-4}$, $1.0 \times 10^{-2}$, and $1.0 \times 10^{-1}$ for Si(111), MLM1 and MLM2, respectively; 2) a flux of $2 \times 10^{9}$, $1 \times 10^{11}$, and $4 \times 10^{11}$ photons/s, for Si(111), MLM1, and MLM2, respectively at 15 keV and 100 mA; and 3) spot sizes ranging between 2 µm × 2 µm and 4 µm × 4 µm (vertical × horizontal). Within this thesis, the VESPERS beamline was used to collect the Au and Hg L$_3$-edge XANES data from the daguerreotype test plate, which is examined in Chapter 3.

![Figure 2-4 Layout of VESPERS beamline at the CLS](image)

2.1.2 Cornell High Energy Synchrotron Source

The Cornell High Energy Synchrotron Source (CHESS) is located at Cornell University, Ithaca, New York. Located beneath an athletic field, the Cornell Electron-positron Storage Ring has a circumference of 768 m, a storage ring of 5.3 GeV, and operates at a current of 125 mA. After a recent upgrade that involved the installation of two, 150 cm long compact undulators in the West flare, which feeds both the A- and G-lines, CHESS is now the 5$^{th}$ high-energy storage ring synchrotron in the world to be classified as 3$^{rd}$ generation [8]. Depending on the beamline, a range of optics are used at CHESS, such as diamond monochromators for undulator beamlines, high-resolution Si monochromators for spectroscopy experiments, and wide-bandpass multilayer optics for experiments that require high-flux. Table 2-2 outlines the contributions of the CHESS beamlines and endstations to this thesis.
Table 2-2 Summary of CHESS beamline facilities included in this thesis.

<table>
<thead>
<tr>
<th>Endstation and Beamline</th>
<th>Energy Range (eV)</th>
<th>Thesis Work</th>
<th>Chapter</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1 at CHESS</td>
<td>19 900 – 32 500</td>
<td>Rapid scanning XRF imaging of full plates post-cleaning</td>
<td>Chapter 6</td>
</tr>
<tr>
<td>G3 at CHESS</td>
<td>8000 – 13 600</td>
<td>Rapid scanning XRF imaging of full plates pre-cleaning</td>
<td>Chapter 5 &amp; 6</td>
</tr>
</tbody>
</table>

2.1.2.1 A1 Beamline

The A1 beamline comes from a 1.5 m compact undulator source and operates at a photon energy of 19.9 keV and 32.5 keV [9]. While techniques such as ultra-small angle X-ray scattering, wide-angle X-ray scattering, and general XRD with reciprocal space mapping are available at the A1 line, the work in this thesis focuses on its XRF mapping capability (spatial resolution 30 µm \( \times \) 30 µm). The beam size at the sample can reach a maximum size of 1 mm \( \times \) 4 mm (vertical \( \times \) horizontal) and a minimum of 30 µm \( \times \) 30 µm (vertical \( \times \) horizontal) using a focusing capillary. Typical operating conditions include: 1) a flux of 2 \( \times \) 10^{12} photons/s at 19.9 keV and 2.3 \( \times \) 10^{11} photons/s at 32.5 keV; 2) an energy resolution \( (E/\Delta E) \) of 1000; and 3) the use of a side-bounce diamond Laue (111) and (220) monochromator, a vertical bendable X-ray mirror (focusing, harmonic rejection), and micro-focusing capillaries. Chapter 6 contains the XRF data from 19th century daguerreotypes that was collected at this beamline.

2.1.2.2 G3 Beamline

Sourced from the positron beam, the G3 line at CHESS has an energy range of 8 – 13.6 keV and is fed by two 1.5 m compact undulators. The G3 beamline uses two double-crystal multilayer monochromators to deliver the beam with a flux of \( \sim 6 \times 10^{13} \) photons/s (at 10 keV) in a 2 mm \( \times \) 1 mm spot size and a bandwidth \( \Delta E/E \) of 1.5% [10,11]. A narrower bandwidth can be achieved by an in-hutch, channel-cut Si(111) monochromator for on-the-fly measurements. G3 is located at the end of the G-line and is
equipped with a ultrahigh vacuum diffractometer for in situ growth studies of oxide thin films by pulsed laser deposition. This feature of G3 is beyond the scope of this thesis. Rapid scanning XRF capability is achieved with the 384-element Maia detector [12], which operates in backscatter geometry [13]. Equipped with an array of 384 individual Si PIN diodes, the Maia detector allows for real-time imaging, processing and/or spectral deconvolution at photon rates exceeding $10^7$ counts per second and 50 µs per pixel [12]. The sensitivity for trace element examination is significantly enhanced through the use of the Maia detector and allows for the collection of (relatively) larger areas to be scanned in high definition in much shorter time intervals. The rapid scanning XRF data collected from this beamline is presented and discussed in Chapter 5 and 6.

2.2 Synchrotron Techniques

2.2.1 X-ray Absorption Spectroscopy

In this thesis, X-ray absorption spectroscopy (XAS) was one of the primary synchrotron techniques utilized to examine the daguerreotype surface. XAS is based on the partial or total absorption of X-rays by matter, with the absorption/attenuation of the X-ray following the Beer-Lambert law (equation 2-1):

$$I_t = I_0 e^{-\mu t}$$

(2-1)

where $I_0$ is the intensity of incident X-ray, $I_t$ is the transmitted light intensity, $t$ is sample thickness, and $\mu$ is the absorption coefficient. The absorption coefficient, which is highly correlated with both atomic number ($Z$) and X-ray energy ($E$) of a core electron, can be written as (equation 2-2):

$$\mu \approx \frac{\rho Z^4}{AE^3}$$

(2-2)

where $\rho$ is the sample density and $A$ is the atomic mass. The X-ray absorption cross section ($\sigma$) can also be used to describe $\mu$ (equation 2-3):

$$\mu = \sigma \cdot \rho$$

(2-3)
When the incident X-ray is equal to or greater than the binding energy (BE) of a core electron, a sharp increase of the $\mu$ results. This abrupt rise is called the absorption edge, and is due to the substantial escalation in the number of absorbed photons from the increase of the absorption cross section (equation 2-3). Figure 2-5 shows the atomic absorption cross section as a function of X-ray energy ($E$). Several absorption edges are included in Figure 2-5, which are named according to the origin of the excited electron. For the case of Hg, the excitation of the 1s (K-shell), 2s (L$_{1}$-shell), 2p$_{1/2}$ (L$_{2}$-shell), and 2p$_{3/2}$ (L$_{3}$-shell) electron produce the Hg K-edge, L$_{1}$-edge, L$_{2}$-edge, and L$_{3}$-edge, respectively.

For atoms in a chemical environment, the modulations in the $\mu$ above the edge (i.e., with increasing energy) reflect the interactions (either single or multiple scattering) of the outgoing electrons with the neighbouring atoms. This produces various fine structures and is referred to as X-ray absorption fine structure (XAFS).

![Figure 2-5](Image)

**Figure 2-5** Log-log plot of X-ray absorption cross section ($\sigma$) of mercury as a function of X-ray photon energy ($E$) [14].
XAFS can be divided into two regions, the X-ray absorption near edge structure (XANES) and the extended X-ray absorption fine structure (EXAFS) (Figure 2-6). The interpretation of these two regimes differs, as the electron scattering behaviour of atoms is dependent on the kinetic energy (KE) of the electrons. Within the near region (~20 eV below to ~50 eV above the absorption edge) the XANES process takes place. The modulations in the $\mu$ within this region are primarily caused by electronic transitions to bound and quasi-bound states and multiple scattering interferences from neighbouring atoms. Information on the local, chemical environment of the absorbing atom including oxidation states, unoccupied electronic states, and local symmetry [15] can be extracted from the XANES region. When the outgoing electron has a much higher KE, single scattering is the dominant process. This higher energy range, from ~50 eV to ~1000 eV above the edge, is where the EXAFS process occurs. Information on local structures including bond length and coordination number within the first two or three atomic shells can be extracted from this region [16]. The work in this thesis is primarily focused on the XANES region of the XAFS process. Further detail on this process in discussed below.

![Image of a normalized absorption spectrum showing pre-edge, XANES, and EXAFS regions.](https://example.com/figure2-6.png)

**Figure 2-6** Example of a normalized absorption spectrum (Cu metal K-edge) with pre-edge, XANES, and EXAFS regions indicated [17].
The X-ray absorption ($\mu$) process can theoretically be described using a single electron approximation. When a core electron undergoes excitation due to the annihilation of an incoming X-ray, it undergoes an electronic transition between initial and final quantum states and leaves the remaining unexcited N-electrons with a core hole. The probability of this electronic transition process, in theory, can be described by Fermi’s golden rule (equation 2-4) where $\psi_i$ and $\psi_f$ are the initial and final state functions, $E_f$ is the eigenvalue for the final state, and $H$ is the interaction Hamiltonian.

$$
\mu(E) \propto \left| \langle \psi_i | H | \psi_f \rangle \right|^2 \cdot \rho(E_f) 
$$

In XANES, the dipole transition (i.e., 1s to p, 2p to s + d, etc.) is the primary contribution and follows the dipole selection rule ($\Delta l = \pm 1, \Delta j = \pm 1,0$). The second contribution, the quadrupole component ($\Delta l = \pm 2,0$), is significantly weaker (on the order of several orders of magnitude). These quadrupole transitions (e.g., 1s to 3d) however, can play an important role, such as in the production of weak oscillation before the main absorption edge (i.e., pre-edge features) due to its high sensitivity to d electron-ligand hybridization in the K-edge XANES of transition metals [18].

As mentioned above, when the energy of the incident X-ray is equal to or greater than the absorption threshold of the element of interest, a core electron is promoted to previously unoccupied quasi-bound and bound states. The differences between the outgoing waves of a free atom and an atom from a diatomic system (i.e., an atom in a chemical environment) are presented in Figure 2-7. In the free atom system (Figure 2-7A), once the incident X-ray has an energy ($E$) equal to or higher than the BE of the core-level electron ($E_0$), a photoelectron is produced. This photoelectron travels as a wave with a wavenumber that is proportional to $\sqrt{(E - E_0)}$. As there are no neighbouring atoms to scatter the photoelectrons in a free atom environment, the absorption coefficient ($\mu$) decreases monotonically after the edge jump. In contrast, the outgoing photoelectron wave that is produced by the absorbing atom in a diatomic system (Figure 2-7B) interacts with, and is subsequently scatter by, the neighbouring atoms, creating multiple scattering pathways.
The resulting constructive and destructive interference between the outgoing and backscattered waves produce modulations in the $\mu$ and are observed as oscillations in the XANES spectrum (see Figure 2-6). As these modulations are the result of several individual scattering pathways, the total absorption coefficient is used to describe these multi-scattering environments (equation 2-7):

$$\mu(E) = \mu_0[1 + \sum_{n \geq 2} \chi_n(E)]$$

(2-5)

Where $\mu_0$ is the absorption coefficient of the absorbing atom and $\chi_n(E)$ is the multi-scattering term from all pathways involving $n - 1$ neighbouring atoms. An example of the multiple scattering processes for $n$ different values can be seen in Figure 2-8.

![Figure 2-7 Schematic of the outgoing photoelectron wave produced by (A) a free atom and (B) a diatomic system upon X-ray absorption and the corresponding XANES spectrum [19].](image)
In this thesis, the L$_3$-edge (a p to d transition) for both Ag and Au was selected to provide further information regarding the Ag-Au alloy that resides on the daguerreotype surface. As the L$_3$-edge probes unoccupied states, which are primarily composed of d-character, insight into charge transfer as a result of alloying can be attained. Such subtle variations cannot be observed with the K edge, which provides information on s to p transitions. However, the K-edge was used to provide surface sensitive information regarding the tarnish of S and Cl observed on the daguerreotype surface. Probing the s to p transition enabled previously unoccupied states of both S and Cl (i.e., to determine the presence of Ag$_2$S and AgCl, respectively) to be elucidated.

### 2.2.2 De-excitation Process

Once the absorption process promotes a core electron to a previously unoccupied state or the continuum, several de-excitation processes can take place to fill the core hole. These de-excitation processes can be either non-radiative (i.e., the ejection of Auger electrons) or radiative (i.e., the emission of XRF). These two processes are shown in Figure 2-9B and Figure 2-9C. In the Auger process, when an electron fills a core hole, non-radiative energy is subsequently released and is transferred to a third electron, which is excited into the continuum. The emission of XRF (a radiative process) occurs in one-step where an electron from a higher shell relaxes down to fill the core hole. As both processes are
correlated to the creation of a core hole from the X-ray absorption process, the Auger and X-ray fluorescence yield are proportional to the absorption coefficient ($\mu$) of the element of interest in a XANES measurement. They are also a competing process (i.e., Auger yield = 1 (total decay) – fluorescence yield). Figure 2-9D shows how with higher atomic number ($Z$), fluorescence is the principal de-excitation process while with lower $Z$ elements, the Auger decay process is predominant [20].

![Diagram of de-excitation processes](image)

**Figure 2-9 Illustration of the de-excitation processes where open circles represent holes and solid circles represent electrons. (A) Photo-absorption of incident X-ray ($hv$) producing a photoelectron and a core hole. (B) The Auger, and (C) X-ray fluorescence de-excitation processes. (D) Plot of fluorescence yield as a function of atomic number for K and L shells [20].**

In this thesis, fluorescence yield (FLY) is the primary detection mode used to measure XAFS. While the probing depth of FLY depends on the energy of the incident photon beam (along with other factors), FLY is considered a “bulk” sensitive technique as it has a relatively deeper penetration depth (i.e., hundreds of nanometers to a micron in depth) when compared to other “surface sensitive” methods, such as total electron yield (TEY), which has a probing depth of ~5 nm. FLY relies on the assumption that the yield is proportional to the absorption coefficient ($\mu$). Therefore, if the sample is too thick or too concentrated with a specific element, self-absorption may occur, leading to partial, or total, inversion of the FLY spectra. This may occur if the sample is thicker than one absorption length (i.e., the distance over which the incident X-ray intensity is reduced by
a factor $1/e$). However, concentrated samples do not necessarily lead to peak broadening due to self-absorption. For concentrated samples, self-absorption can be minimized by ensuring the sample is thin enough. Self-absorption differs from saturation, which depends on the detector and can be partially mitigated by varying acquisition time, slit size, and the presence of filters.

### 2.2.3 X-Ray Fluorescence Imaging

Along with XAFS analysis, synchrotron-based XRF imaging is one of the primary techniques used throughout this thesis. When an electron relaxes to fill a core hole, the emitted fluorescence has an energy that is equal to the difference in energy between the two involved orbitals. As each element has electronic orbitals that have a characteristic energy, like the XAFS process, XRF is element specific. For example, the $L_{\alpha_1}$ emission lines for Au and Hg are 9713 eV and 9988 eV, respectively [21]. The wavelength ($\lambda$) of the fluorescence photon can be determined from Planck’s Law (equation 2-8) where $h$ is Planck’s constant ($6.63 \times 10^{-34}$ J s), $c$ is the speed of light in a vacuum ($3.00 \times 10^8$ m s$^{-1}$), and $E$ is the photon energy.

$$\lambda = \frac{hc}{E} \quad (2-6)$$

At a synchrotron facility, a monochromator is often used to select a specific energy prior to focussing the X-ray beam onto the sample. Spot sizes for microprobes range from 1 – 10 µm while nanoprobes can achieve 50 – 500 nm. The sample is then translated through the beam by means of a motorized stage (in the XYZ directions) in a raster pattern. This produces an XRF image based on distinct fluorescent X-rays emitted via the photoelectric effect. A detector, which is commonly positioned either in backscatter geometry or perpendicular to the incident beam, quantifies the fluorescence X-rays. Which X-rays are detected depends on a variety of factors: 1) the configuration of the experiment, 2) the capabilities of the beamline, and 3) the energy selected. Typically, XRF imaging can be done over an energy range of 2 – 25 keV. Soft X-ray experiments are normally conducted under vacuum using a SDD. This was the case for the XRF imaging work that was conducted at the SXRMB beamline at the CLS. Conversely, the rapid scanning XRF mapping that was collected at A1 and G3 beamlines at CHESS were accomplished with
hard X-rays using a solid-state detector and a fast, dynamic Maia detector at the A1 and G3 lines, respectively. This work was done under atmospheric conditions.

Synchrotron-based XRF offers ppm levels of detectability for many elements [22]. Elemental maps can be converted to yield quantitative images / local compositional values through the use of various calibration models. Quantitative elemental analysis was not conducted in this work due to the extreme variation between the plates examined in this study.

2.2.4 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is a surface sensitive technique that provides quantitative information on the elemental composition of a specimen of interest. This is done by irradiating a material with X-rays under vacuum and measuring the kinetic energy (KE) and the number of electrons emitted from the sample within the first 10 nm. When an atom on the sample surface absorbs an X-ray, a single electron is ejected from the inner shell and the KE is measured using an electron energy analyzer (Figure 2-10). The binding energy (BE) of the detected ionized electron is determined through using the following relation:

\[ KE = h\nu - BE - \phi \]  

(2-7)

In equation 2-9, \( h\nu \) is the incident X-ray and \( \phi \) is the work function, which is the minimum energy required to move an electron to the vacuum level from the sample (Figure 2-10). If the sample is grounded, the sample and spectrometer Fermi Level equalizes upon contact. The resulting spectrum is a presentation of the measured photoelectron intensity versus the binding energy of the detected electrons. The area under the curve of each peak at each specific BE is directly proportional to the amount of the particular element within the irradiated sample volume and photoionization cross-section (\( h\nu \) dependent).
While the surface sensitivity of lab XPS is well suited to the study of various surfaces, synchrotron-based XPS has the ability to use high-energy (HE) X-rays to probe an order of magnitude deeper under the surface, which is not achievable by lab XPS without destructive ion sputtering. This is done by increasing the energy of the incident X-ray with HE-XPS, which in turn increases the KE of the photoelectrons. As the inelastic mean free path (IMFP) is a function of the KE, an increase of incident energy would cause an increase in escape depth as it follows the universal curve for IMFP (Figure 2-11). Laboratory-based XPS can provide depth information by surface ablation using ion-sputtering techniques at a fixed X-ray energy. In this thesis, both HE- and laboratory-based XRF were used to quantify at the surface and sub-surface of two daguerreotype test plates. This work is discussed in Chapter 3.
2.3 Scanning Electron Microscopy

Scanning electron microscopy (SEM) can provide information regarding surface topography of a sample. A fine focal point at the surface (~0.4 – 5 nm) is achieved by focusing a high energy electron beam with one or two condenser lenses while under vacuum. The energy of the incident beam typically ranges from 1 to 30 keV. This beam is rastered across the surface both horizontally and vertically over a rectangular area of the sample [24]; the subsequently scattered electrons are detected.

The interaction of the incident electron beam with the sample surface produces a variety of energy loss mechanisms. Secondary electrons, due to their low energy (< 50 eV) are produced from the first few nanometers of the sample surface and provide information on surface topography. The result is a brightness contrast map where higher elevations appear brighter and deeper areas appear darker; this is the result of the proximity of these inelastically scattered electrons to the detector. Due to this being a lower energy process, the production of secondary electrons is more probable with lower Z elements. Chemical differentiation is attained through the collection of backscattered electrons. These high

![Figure 2-11 Universal curve for the inelastic mean free path as a function of kinetic energy for synchrotron radiation [23].](image)
energy electrons are produced through elastic scattering interactions from the incident electron beam and the specimen. As high Z elements backscatter electrons more strongly than low Z elements, heavy elements appear brighter and lighter elements appear darker in the resulting image.

When the focused electron beam interacts with the specimen, electrons within the sample can be excited to a previously unoccupied state. The relaxation process to fill the core hole releases discrete X-rays that are element and energy gap specific. The detection of these X-rays is called energy dispersive X-ray (EDX) spectroscopy.

For this thesis, SEM-EDX served many roles over the course of this study: 1) to show the physical structure of image particles in different regions (i.e., highlight, midtone, and shadow), 2) to provide chemical information across the daguerreotype surface, and 3) to semi-quantitatively determine the image particle density of the highlight, midtone, and shadow areas. SEM-EDX was used both before and after synchrotron analysis to document any variations to the daguerreotype image particles as a result of SR analysis. SEM-EDX is not an ideal form of documenting damage to the daguerreotype surface (aside from tracking any changes to image particle integrity, especially after electrocleaning treatment, see Chapter 6) as it is not obvious that SEM-EDX is no less damaging that SR analyses. Optical examination was therefore also used to qualitatively track any changes to the daguerreotype surface.

2.4 Electrocleaning

Preliminary localized electrocleaning experiments were conducted on all plates prior to full plate cleaning. Full plate treatment was conducted in collaboration with John McElhone at the National Gallery of Canada (NGC). The analysis of the potentiodynamic data that was collected in the preliminary localized cleaning efforts is beyond the scope of this thesis.

By applying an external power source, corrosion on the daguerreotype surface can be removed. The electrocleaning process requires the plate to be immersed in an electrolyte (an electrically conductive solution), which allows charge to flow between the
daguerreotype (the working electrode) and the platinum (Pt) wand (the counter electrode). By manipulating the current (flow of electrons) and the potential (electric pressure) between the Pt counter electrode and the daguerreotype, the surface tarnish can be removed. When the proper parameters are chosen, this conservation treatment can return the daguerreotype to (or very close to) its original state.

Two different methods were used in this study: the Barger process [25] and the Wei process [26]. In the original procedure put forward by Barger et al., an external current was applied to the daguerreotype with a movable aluminum electrode while placed in a 0.08 M ammonium hydroxide electrolyte solution (NH$_4$OH; pH = 12). The use of the Pt wand was later introduced, as it was observed that the more noble the counter electrode, the better the cleaning results. Altering the potential of the daguerreotype between anode and cathode in repeated cycles resulted in a substantial removal of surface tarnish. The plate was then rinsed and dried. While no negative alterations to the surface have been identified, alternate methodologies have been proposed [27-29]. One such study, proposed by Wei et al. [26], applied only a cathodic potential to avoid the oxidation of silver on the surface. This was conducted in an electrolyte solution of 0.1 M sodium nitrate (NaNO$_3$; $\sim$ pH = 6). All plates were subsequently examined with SR-XRF. This work is discussed in Chapter 6.

2.5 References


Chapter 3

The important thing is to never stop questioning.

Albert Einstein, theoretical physicist (1879 – 1955)

3 The Application of XANES and XPS to the Daguerreotype Surface

3.1 Introduction

In this chapter, XANES spectroscopy and XPS, from both synchrotron and laboratory sources were used to examine daguerreotype test plates. This was done to 1) collect information regarding the chemical distribution and speciation both on the surface and with depth and 2) to provide quantitative chemical information and oxidation states of the elements of interest. Importantly, performing SR analysis on the two test plates would ensure that this process does not induce any negative alteration to the surface, confirming that this analytical technique would be appropriate for the examination of historic daguerreotypes. SEM provided microstructure information of select areas for both techniques. While XANES was applied to historic daguerreotypes, discussed in Chapter 4 and 5, XPS was only used in the examination of the test plates due to sample size; XPS provided information regarding the Ag-Au alloy on the surface and the near surface. This XPS work provides information regarding the physical and chemical structure that can subsequently be applied to the 19th century plates.

*A version of this chapter has been published in *Can. J. Chem.* 2017, 95 and *Int. J. Conserv. Sci.* 2017, 8.*
3.2 Materials and Methods

3.2.1 Sample Selection and Preparation

The daguerreotype plates (5 × 1 cm) used in this study (Figure 3-1A) were prepared by Dr. Michael Robinson at Century Darkroom, Toronto using the process described by Humphrey [1].

The samples were produced using silver-clad copper plates; the thickness of Cu and Ag (99.9% purity) layers were ~ 475 – 600 µm and ~ 10 – 16 µm, respectively. The plates were polished using 3m abrasive papers and Nushine II grade S Nuvite polishing paste until a mirror finish was achieved. The plates were subsequently washed with soap and water and, when dry, rubbed with velvet and alcohol. Buffing with cotton velvet covered paddles, first with rouge powder (iron oxide) then with carbon black powder with a second buffing paddle, completes the polishing process.

![Figure 3-1 Optical images of (A) full daguerreotype test plate and (B) close up of examined area with labelled regions of interest (A1: dark region; A2: midtone region; A3: bright region).](image)

The plates were then made light sensitive using halogen vapours. The polished plate was first placed over iodine crystals contained within a sealed box at room temperature where it remained until it attains a yellow colour. The same process is repeated over a mixture of bromine and chlorine crystals, which serve as the source for the bromine and chlorine vapour, until a deep yellow/red colour is achieved. A final exposure to iodine vapour was then conducted under non-actinic light to ensure no pre-mature exposure of the plate. The time required at each sensitizing step depends on 1) the chemical concentration, 2) the
room temperature, and 3) the expertise of the producer as the process is judged by inspection.

The plate is then exposed in a camera to daylight illumination (i.e., the image of interest).

Subsequent development is conducted by exposing the plate to mercury vapour heated to 70 °C for 7 minutes (time and temperature can be altered for aesthetic purposes). Residual silver-halides were removed from the plate through a fixing process with a solution of thiosulphate pentahydrate until the magenta colour of the plate dissolves away. Finally, the plate is toned with a gold chloride solution that is comprised of two parts (Part A and Part B), which is orange in colour when first mixed but clears in ~ 2 hours. To reduce the clearing process to 5 minutes, 20 drops of a third solution (Part C) are added and immediately filtered after mixing.

Part A: 10 mL of 0.2% w/v of HAuCl₄•H₂O

6 drops of 2% w/v solution of sodium metabolite

Part B: 10 mL of 1% Na₂S₂O₃

Part C: 3.8 g of NH₄Cl

3.2 g of NaCl

60 mL of DI H₂O

The gold toner was poured onto the plate, which was supported, leveled, and heated with an alcohol lamp from below. This process took 2 minutes. The plate was rinsed with deionized water and dried. The plates were stored and placed in a container to prevent surface abrasion. The plates were used as received.

3.2.2 X-ray Absorption Near Edge Structure

All reported XANES spectra were taken at the labeled locations on the test plate (A1: dark region; A2: midtone region; A3: bright region) (Figure 3-1B).
Three separate beamlines at the Canadian Light Source (CLS) were used to collect the absorption data: SXRMB, VESPERS, and HXMA (Table 3-1). The beamlines were selected as their respective energy ranges corresponded to the absorption edges of the elements of interest (Ag, Au, Hg, and S). SXRMB was utilized to collect the Ag L₃-edge XANES. The beam was monochromatized by a Si(111) double crystal monochromator and XANES were recorded in the FLY mode using a 13-element Ge detector situated at 45° with respect to the sample stage. Spectra were collected from 3331 eV to 3411 eV using a 2.00 eV step size before, a 0.20 eV step size at, and a 0.75 eV step size after the L₃ absorption edge region. Larger step sizes before the edge are chosen so that appropriate background correction can be conducted; a smaller step size is used at the edge to optimize the quality of the data. Step size was chosen based on monochromator and slit resolution. The size of the beam on the sample was 1 × 4 mm (vertical × horizontal).

<table>
<thead>
<tr>
<th>Element</th>
<th>Beamline</th>
<th>Edge(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>SXRMB (BM, 1.7 – 10 keV) (daguerreotype test plate; Ag-Au alloy, AgCl, and Ag₂S standards)</td>
<td>L₃,₂-edge</td>
</tr>
<tr>
<td>Au</td>
<td>VESPERS (BM, 6 – 30 keV) (daguerreotype plate)</td>
<td>L₃,₂-edge</td>
</tr>
<tr>
<td></td>
<td>HXMA (Wiggler, 5 – 40 keV) (Ag-Au alloy standards)</td>
<td></td>
</tr>
<tr>
<td>Hg</td>
<td>VESPERS (daguerreotype plate)</td>
<td>L₃-edge</td>
</tr>
<tr>
<td>S</td>
<td>SXRMB (daguerreotype plate)</td>
<td>K-edge</td>
</tr>
</tbody>
</table>

The SXRMB line was also used to collect the S K-edge over an energy range of 2454 eV to 2534 eV with a 2.00 eV step size before, 0.20 eV at, and 0.75 eV after the absorption edge. The size of the beam on the sample was 1 × 4 mm (vertical × horizontal). The Au and Hg L₃-edges were examined on the VESPERS beamline in FLY with a microbeam using KB mirrors. The Au L₃-edge XANES spectra were collected from 11 759 eV to 12 150 eV with a step size of 10.00 eV before, 0.50 eV at, and 0.05 eV after the
absorption region. The Hg L₃-edge was collected over an energy range of 12 124 eV to 12 400 eV with the same step size variations as the Au L₃-edge. The metallic Hg(s) standard was collected in FLY; the preparation for this standard is outlined in detail elsewhere [2].

A series of Ag-Au alloy standards (Table 3-2), whose preparation is outlined in Bzowski et al. [3], were also analyzed at the CLS. The Ag L₃-edge was collected at the SXRMB line under the same conditions described above. The Au L₃-edge was analyzed at the HXMA beamline that focuses the beam with a liquid nitrogen cooled double crystal Si(111) monochromator (Kohzu CMJ-1). Further collimation is achieved by using a 1.15 m long water-cooled silicon toroidal focusing mirror. The resulting beam size was 1 × 10 mm (vertical × horizontal).

<table>
<thead>
<tr>
<th>Name of Standard</th>
<th>Atomic Percentage of Silver</th>
<th>Atomic Percentage of Gold</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>100%</td>
<td>0%</td>
</tr>
<tr>
<td>Ag₉₅Au₅</td>
<td>95%</td>
<td>5%</td>
</tr>
<tr>
<td>Ag₇₅Au₂₅</td>
<td>75%</td>
<td>25%</td>
</tr>
<tr>
<td>Ag₅₀Au₅₀</td>
<td>50%</td>
<td>50%</td>
</tr>
<tr>
<td>Ag₅Au₉₅</td>
<td>5%</td>
<td>95%</td>
</tr>
<tr>
<td>Au</td>
<td>0%</td>
<td>100%</td>
</tr>
</tbody>
</table>

**Table 3-2 Series of silver-gold alloy standards [3].**

### 3.2.3 Data Processing

The Athena software package [4] was used to calibrate, background subtract, normalize, and average all spectra. The true inflection point at the edge was determined by taking the first derivative of each spectrum, following the procedure outlined by Ravel [5]. These first derivative inflections were 3351 eV, 11 919 eV, 12 284 eV, and 2472 eV for the Ag L₃-edge, Au L₃-edge, Hg L₃-edge, and S K-edge, respectively. A first-order polynomial was fit to the pre- and post-edges of the spectra along with normalizing the edge-jump of
each spectrum to one. When appropriate, the Athena software was used to perform a linear combination fit (LCF) to provide semi-quantitative weight percent (wt. %) values from the normalized $\mu(E)$ daguerreotype spectra in terms of spectra from standards. Here, two or more standard spectra are fit to the spectrum in question, which has already undergone data processing. The standards are constrained to 100% of the unknown by having the weight for the last spectrum be one minus the sum of the other weights. Therefore, if three standards are used, the first two would have weights x and y and the third would have weight 1-x-y. X and y are then varied to obtain an optimal fit. Each standard spectrum is interpolated onto the energy grid of the unknown spectrum when the fit is performed. Analyses were conducted over an energy range of -20 eV below and +30 eV above the edge. Uncertainty is determined through subtracting between the original data and the fitted spectrum. This analysis can determine the species percent contribution of standard in a heterogeneous material. All fits are presented in Appendix F.

3.2.4 X-ray Photoelectron Spectroscopy

The laboratory XPS analysis (Figure 3-2A) was carried out at Surface Science Western, University of Western Ontario, using a Kratos AXIS Ultra XPS and a monochromatic Al K$_\alpha$ X-ray (1486.7 eV, 15 mA, 14 kV, 210 W) with a peak resolution of 0.47 eV (Ag 3d$_{5/2}$). Instrument base pressure was 1.5 – 2 × 10$^{-9}$ torr. Fine spectra were collected from all areas. Survey scan and high-resolution spectra were acquired from 400 × 400 $\mu$m spots using 160 eV and 20 eV pass energies, respectively. CasaXPS version (2.3.14), XPSPeak, and Vision 2 Processing Software was used for data processing [6]. Depth profiles were collected using ion ablation to remove sequential surface layers at each region over a period of 41 minutes for L1 and 35 minutes for L2 and L3. A 4 kV (15 mA) Ar$^+$ ion beam rastered over an area of 3 × 3 mm was used for the depth profiling. The sputter rate was estimated to be 1.8 nm/min based on an Al$_2$O$_3$/Al standard. Due to the varying density of between the Al$_2$O$_3$/Al standard and the Ag daguerreotype plate, the presented depth profiles for Ag represent the upper bound of the depth reached as the calculation is based on a relatively less dense, and lighter metal.
Figure 3-2 Optical images of daguerreotype test plates examined with (A) laboratory-based XPS (L1: bright; L2: midtone; L3: dark) and (B) synchrotron-based XPS (S1: medium bright; S2: dark; S3: bright; and S4: midtone).

The SXRMB (06B1-1) beamline at the CLS was used for the HE-XPS experiments (Figure 3-2B) [7]. Two different excitation energies were used to examine two different depths of the daguerreotype: 3.0 keV and 8.0 keV; these energies lead to a probing depth of ~3 and ~ 6 nm, respectively [8-10], based on the density of pure Ag (the primary material in the plate). The beam was monochromatized by a Si(111) crystal monochromator. The size of the beam on the sample was 4 × 1 mm (horizontal × vertical) in both measurements. A base vacuum of 3.2 × 10⁻¹⁰ torr was maintained. A step size of 400 meV was used for survey scans and a step size of 40 meV for fine scans. The valence band was collected with a step size of 100 meV. The overall energy resolution is ~ 0.6 eV at 3.0 keV and ~ 0.9 eV at 8.0 keV. The IGOR software package (version 6.11) was used to process the collected HE-XPS data [11].

3.2.5 Scanning Electron Microscopy

The scanning electron microscopy (SEM) images of the studied regions on the daguerreotype test plate were obtained using the LEO (Zeiss) 1540XB FIB/SEM instrument at the Western Nanofabrication facility. Topographic imaging was performed at 1 kV with a working distance of 4 mm and backscatter imaging at 10 kV and 9 mm.
3.3 Results and Discussion

3.3.1 Ag L₃-edge XANES

The Ag L₃-edge XANES is shown in Figure 3-3. The oscillation magnitude relative to a smooth background was compared to the alloy standards; in general, the magnitude is sensitive to the scattering characteristics of nearest neighbouring atoms. There is no sharp peak at the rising edge, also known as the whiteline (WL), indicating that the Ag d band is full. The oscillations in the spectra at increasing energy above the threshold (labeled II to V) are due to the multiple and single scattering of the photoelectrons by the neighboring Ag atoms. The oscillation patterns within the L₃-edge XANES of the alloy standard and the A1-3 specimen are indicative of a face centered cubic (fcc) structure [3].

![Figure 3-3 Ag L₃-edge XANES for test plate (A1, A2, A3); alloy standards (Ag, Ag₉₅Au₅, Ag₇₅Au₂₅, Ag₅₀Au₅₀, Ag₅Au₹₅); tarnish standards (AgCl and Ag₂S). The dotted lines track the position of the resonances.](image-url)
Region I is the WL region assigned to the excitation of a 2p\textsubscript{3/2} electron to unoccupied bands just above the Fermi level, which possess both s and d character. The absorption is weak because the 5d bands are full in Ag metal, although the presence of some d character is possible due to s-d hybridization. Regions II – IV can be viewed as multiple scattering resonances resulting from the fcc environment of the Ag atom [3]. The intensity of peak II increases from Ag\textsubscript{5}Au\textsubscript{95} to pure Ag while the magnitude of region V decreases (Figure 3-4A). At peak V and beyond, the electron energy is sufficiently high to be considered as an extended X-ray absorption fine structure (EXAFS) oscillation where single scattering begins to prevail.

![Figure 3-4 Comparison of (A) the Ag L\textsubscript{3}-edge alloy standards and (B) amplification of near edge region for daguerreotype regions A1, A2, A3 against Ag, Ag\textsubscript{95}Au\textsubscript{5}, and Ag\textsubscript{75}Au\textsubscript{25} standards. The dotted lines track the position of the resonances.](image)

The position of the oscillations (positions of the resonance relative to the threshold) can be used to qualitatively infer the degree of Ag-Au lattice distortion in the fcc structure. Au and Ag are comparable in size [12] but different in backscattering amplitude and phase, introducing slight distortions in XANES oscillations in the Ag-Au alloys compared to pure Ag. These multiple scattering events are larger in Au than Ag and
therefore have different $k$ dependence, $k$ being the wavenumber of the photoelectron relating to the square root of the photon energy above the threshold [13]. These factors will influence the oscillations in the XANES spectrum.

The XANES of all the daguerreotype sample areas (Figure 3-4B) (A1 - dark, A2 - midtone, and A3 - bright) look similar to that of pure Ag and Ag$_{95}$Au$_5$ while noticeably different from the alloys with dilute Ag in Au. The A1-3 oscillations of region V have shifted to slightly higher energy when comparing the test plate to the Ag-Au alloy standards, which is indicative of a varying Ag-Au neighborhood surrounding the absorbing atom. Examination of regions I, II, and V from the test plate (A1-3) shows that the magnitude falls between Ag and Ag$_{95}$Au$_5$, indicating that the alloy present within the daguerreotype surface and near surface region has between 95 – 100 atomic percent (at. %) Ag and 5 – 0 at. % Au. Based on the diffusion coefficient of $10^{-13}$ cm$^2$/s calculated for Au into Ag and Ag into Au on a historic daguerreotype plate [14], the observed alloy percentage of relatively low levels of Au may be partly due to the relatively slow inter-diffusion for Ag and Au. However, as the degree of gilding is operator dependent, it is difficult to determine if the degree of alloying is due to the age of the plate or the individual procedure and methodology of the producer.

Due to the overriding signal of the Ag substrate [15], the Ag L$_3$-edge is not appropriate for comparison to the Ag$_2$S and AgCl standards, which bear no resemblance to the daguerreotype regions A1-3. Therefore, the majority of information regarding the subtle variations in chemical structure on the daguerreian surface will come from Au, Hg, and S, which are discussed below, as they provide a more surface sensitive examination. In contrast, due to the materiality of the daguerreotype, the Ag L$_3$-edge provides information from both the bulk and the surface, thereby limiting the amount of attainable surface sensitive information from this absorption edge.

### 3.3.2 Au L$_3$-edge XANES

The Au L$_3$-edge XANES of regions A1-3 and alloy standards are shown in Figure 3-5. Gold is the most electronegative metallic element having a Pauling scale value of 2.54, compared to Ag at 1.93 [16] and, therefore, it is expected that Au will gain charge from
Ag upon alloy formation. It is also expected that Au upon deposition on Ag will form Ag-Au alloys. Previous analysis of the Au L$_3$-edge from Ag-Au alloys established that the WL intensity increases upon dilution of Au in Ag. This result indicates that Au in fact gains s charge ($\Delta n_s > 0$) and loses 5d charge ($\Delta n_d < 0$) upon dilution in Ag. However, the overall charge flow ($\delta$) though small, is from Ag to Au, in line with electronegativity considerations [17].

![Graph showing Au L$_3$-edge XANES from daguerreotype test plate (A1, A2, A3); alloy standards (Ag$_{95}$Au$_{5}$, Ag$_{75}$Au$_{25}$, Ag$_{50}$Au$_{50}$, Ag$_{5}$Au$_{95}$, Au). The dotted lines track the position of the resonances.](image)

The Au L$_3$-edge jump appears at 11 919 eV (region I) and corresponds to the electronic transition from the 2p$_{3/2}$ core level to the vacant 5d$_{5/2}$ and 5d$_{3/2}$ states just above the Fermi
level. From Figure 3-5, information can be gained by closely inspecting the edge jump. It should be noted that although Au has a full d-band, s-d hybridization and electron redistribution upon alloying with Ag will introduce unoccupied densities of states of 5d character at the Fermi level.

From Figure 3-6A we see that as the relative concentration of Au compared to Ag is greatly reduced. This is evident in the gradual increase in the area under the curve at region I from pure Au to the Ag$_{95}$Au$_{5}$ alloy is indicative of relatively more vacant 5d$_{5/2,3/2}$ states. This observation indicates a d charge transfer from Au to Ag upon dilution. The resonances in regions II and III arises from the electron transitions to unoccupied densities of states above the Fermi level (multiple scattering). Peaks at location IV and beyond are EXAFS, arising from bound-to-continuum transitions modulated by single backscattering of neighboring atoms. A closer inspection of region V suggests that the Au L-edge from locations A1-3 is most similar to the Au, Ag$_{75}$Au$_{25}$, and Ag$_{95}$Au$_{5}$ standards [18].

While the magnitude and oscillation frequencies for peaks I and II in regions A2 and A3 (Figure 3-6B) are similar, which closely follows the Au standard, differences in intensity arise in peaks II, II, and IV. This is most likely due to similar image particle characteristics and composition in these two regions (A2 being a midtone and A3 being a bright region). Furthermore, while daguerreotype regions (A1-3) resemble the Au standard oscillations in peaks I and II, variations in the oscillation frequencies and magnitude appear in peaks III – V. This is due to the difference in neighbouring atoms relative to the Au standard and is evidence of the formation of a Ag-Au alloy. A slight increase in area under the WL at peaks I and II may suggest proportionally less 5d charge (i.e., dilution) in regions A1-3 compared to the Au standard. This is most prominent in region A1, suggesting that the greatest degree of alloying occurs in shadow regions and may support the notion that an Ag-Au alloy forms in the subsurface of the daguerreotype plate. Shadow regions contain few or no image particles and thus enable an increased amount of Au to diffuse into the subsurface, thereby allowing for the relative enrichment of Au in the Au-Ag alloy. This is the result of simultaneous diffusion of Au into the Ag substrate and Ag into the Au adlayer [14].
The normalized Au $\mu(E)$ spectra from areas A1-3 were compared to the alloy standards using LCF. Analyses were conducted over an energy range of -20 eV below and +40 eV above the edge, thereby semi-quantitatively fitting the alloy standards to peaks I, II, and III. Region A1 revealed that alloy standards Ag$_{95}$Au$_5$ and Ag$_{75}$Au$_{25}$ were the primary contributors to the spectrum, having weight percent (wt. %) values of 24.9 and 75.1 for Ag$_{75}$Au$_{25}$ and Ag$_{95}$Au$_5$, respectively. A similar result was observed in region A2, which contained Ag$_{75}$Au$_{25}$ and Ag$_{95}$Au$_5$ wt. % values of 27.0 and 73.0, respectively. While the LCF curves are a very good fit to the A1 and A2 spectra, it is expected that other Ag-Au alloys are present. Given the spot size of the area analyzed and the diffusion mechanism, a good estimation of the average alloy composition present within the shadow and midtown regions is the average of these two standards: Ag$_{90}$Au$_{10}$.

While regions A1 and A2 only exhibit contributions from Ag$_{95}$Au$_5$ and Ag$_{75}$Au$_{25}$ (i.e., all other alloys had an wt. % of 0 in the LCF report), region A3 had contributions from
Ag_{50}Au_{50} (17.7 wt. %), Ag_{75}Au_{25} (27.7 wt. %), and Ag_{95}Au_{5} (54.6 wt. %). This LCF curve is a very good fit to the A3 spectrum. Again, following the simultaneous diffusion mechanism of Ag into Au and Au into Ag, the proposed alloy for the highlight region is an average of the three contributing standards: Ag_{73}Au_{27}. While these calculations are semi-quantitative at best, it does indicate a significant increase in Au content in the high particle density regions. The amount of Au in the Ag-Au alloy on the daguerreotype test plate increases from dark (A1) to highlight (A3) regions, emphasizing that alloying occurs on both the image particles as well as with depth on the daguerreotype plate. From this, it is suggested that the highlight region(s) (A3) has alloys with higher Au content whereas the Ag-Au alloys in the shadow region(s) (A1) has a relatively lower concentration of Au. This increase in the relative concentration of Au in the highlight regions is most likely due to the increase in surface area in these high particle density areas. In comparison, shadow and midtone regions where few/no image particles are observed have a comparatively smaller surface area and therefore report a lower concentration of Au on the surface.

### Hg L\textsubscript{3}-edge XANES

The Hg L\textsubscript{3}-edge spectra are displayed in Figure 3-7. The absence of a WL indicates the deficiency of d vacancies above the Fermi level indicative of metallic Hg. Peak positions of regions I-IV confirm the presence of an Hg-Ag amalgam particle [2,14,19], which as previously been reported to have 10.5 at. % of Hg [19]. Peak III, IV, and the subsequent EXAFS oscillations, also show characteristics consistent with the Hg-Ag interaction [2]. The slight variations in the EXAFS oscillation from region to region and the multiple undulations indicate that Hg has Hg, Ag, and/or Au neighbours. It is unclear from these spectra if there is any variation in Hg-Ag alloying across the three examined regions. In all likelihood, a variety of Hg-Ag structures are present on the surface as suggest by Ravines et al. [19].
Figure 3-7 Hg L\textsubscript{3}-edge from daguerreotype test plate (A1, A2, A3) in comparison to elemental Hg standard. The dotted lines track the position of the resonances.

3.3.4 S K-edge XANES

The S K-edge (Figure 3-8), which arises from an electron being excited from a 1s orbital to a 3p orbital, was recorded at 2469.5 eV, indicative of transition-metal sulfides, such as Ag\textsubscript{2}S [20,21]. Li et al. [22] have conducted extensive analysis of the edge peak shift as a function of oxidation states, which spans 10 – 12 eV and includes sulfides (2-), native sulfur (0), sulfite (4+), and sulfates (6+). This metal-sulfur bond, specifically a transition metal interaction with S, is confirmed by the double feature at peak I [23]. What differs across A1-3 is the distinction of this peak I, which is greatest in A2 while A1 and A3 appear as a shoulder. The location of the electronic transition of peak III (2482 eV) is due to the presence of sulfates, most likely in the form of Ag\textsubscript{2}SO\textsubscript{4} [21,24], or less likely an organic sulfonate species [25]. The amplitude of this peak decreases from A2 (medium), A1 (dark) to A3 (highlight). A shift in peak position by approximately -0.2 eV for A2 and A3 suggests a different chemical environment in these regions. This may be the result of an Ag\textsubscript{2}S-nanoparticle interaction in these relatively brighter regions [26]. The broad
nature of the peak at ~2500 eV arises from the cumulative multiple scattering contributions of all S species [27]. The source of S is most likely environmental, possibly in the form of an organic S compound or more likely H₂S [28].

![Graph showing sulfur K-edge of daguerreotype plate (A1, A2, A3) with Ag₂S standard. The dotted lines track the position of the resonances.]

3.4 XPS Analysis

3.4.1 Laboratory-Based XPS Results

Depth profile scans accomplished through ion ablation with laboratory-based XPS shows how the elemental composition varies with depth. For location L1 (bright area), Figure 3-9 suggests that the adventitious C signal falls rapidly to a low value around 1.8 nm, after which it increases to a somewhat higher value around 3.6 nm. Subsequently, the C signal then falls to near zero at a depth of 16 nm. The rise around 3.6 nm corresponds to a small drop in the Ag observed in this location. The result may be consistent with the presence of residual carbon black powder from the polishing step during the test plate’s production. After the removal of C on the sample surface, apparent maxima appear for
Ag (3d$^{5/2,3/2}$), Au (4f$^{7/2}$), Hg (4f$^{7/2}$), Cl (2p$^{3/2,1/2}$) and I (3d$^{5/2,3/2}$) before the surface is sufficiently cleaned that the Ag substrate yield approaches 100%. Representative depth spectra for area L1 (bright) is shown in Figure 3-9. The maximum at. % values and associated depths for each element of interest are presented in Table 3-3.

![Figure 3-9 XPS spectra of L1 (bright region) to a depth of (A) 45 nm and (B) 20 nm.](image)

Table 3-3 Maximum atomic percent and the associated depth for each element of interest at the three regions studied.

<table>
<thead>
<tr>
<th>Element</th>
<th>Area L1 - bright</th>
<th>Area L2 - medium</th>
<th>Area L3 - dark</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Maximum Atomic (%)</td>
<td>Depth (nm)</td>
<td>Maximum Atomic (%)</td>
</tr>
<tr>
<td>Ag</td>
<td>100</td>
<td>45</td>
<td>100</td>
</tr>
<tr>
<td>Au</td>
<td>19.0</td>
<td>8</td>
<td>17.5</td>
</tr>
<tr>
<td>Hg</td>
<td>0.9</td>
<td>&lt; 2</td>
<td>0.3</td>
</tr>
<tr>
<td>Cl</td>
<td>--</td>
<td>--</td>
<td>0.7</td>
</tr>
<tr>
<td>I</td>
<td>0.4</td>
<td>&lt; 2</td>
<td>0.4</td>
</tr>
</tbody>
</table>
Depth profiles for each element can be seen in Figure 3-10. While there are distinct maxima in each of the Au depth profiles, the Au appears to persist to a depth of at least 45 nm. The simultaneous rise of the Ag and Au signal is consistent with the formation of an Au-Ag alloy, which remains relatively uniform within the first 12 nm. Mercury appears to be confined to the immediate surface and to be more abundant in the highlighted areas (L1), corresponding to the increased density of Ag-Hg image particles in these regions.

Figure 3-10 Depth scans for Ag, Au, Hg, I, Cl, O, and S at all regions studied (L1 - bright, L2 - medium, L3 - dark).

Oxygen, Hg, Cl, S, and I were present within the first 2 nm and were not detected after 30 minutes of etch time. Surface I is detected in all areas at low concentration and is possibly the result of incomplete removal of the original AgI (used in the sensitizing step). Chlorine was detected in area L2 (medium) and L3 (dark) but not in L1 (bright). As
with AgI, this may be the result of incomplete removal during the thiosulfate wash portion of the plate’s production. The presence of S at the surface could be the remnants of the thiosulfate solution and/or an environmental contaminant. Little tarnish is present on this test plate due to the fact that analysis was conducted shortly after plate production. Therefore, S was not a focus for this portion of the study due to its limited quantity on the surface. Although the origin of Si is unclear, it may be due to the polishing process (the presented sample was polished with 3m abrasive papers and Nuvite polishing paste) or a thin Si contaminant layer.

Figure 3-11 Laboratory-based XPS Hg fine scans and SEM images collected from the daguerreotype test from area (A) L1: bright; (B) L2: medium; and (C) L3: dark. In Figure 3-11, fine scans of Hg are shown alongside their respective SEM images. The observed Hg binding energies (BE) for regions L1-3 are shown in Table 3-4. The least amount of Hg was observed in area L3 (dark) and can be attributed to the lack of image
particles in this region. Conversely, the greatest amount of Hg was observed in region L1 (bright), correlating to the highest density of image particles. As L3 lies on the edge of the plate, a lower halogen and Hg concentration is expected; Ag and Au will be the primary elements present.

**Table 3-4 Binding energies for Hg 4f\textsubscript{7/2} and 4f\textsubscript{5/2} alongside proposed Hg sources.**

<table>
<thead>
<tr>
<th>Area</th>
<th>4f\textsubscript{7/2} Peak Location (eV)</th>
<th>4f\textsubscript{5/2} Peak Location (eV)</th>
<th>Proposed Source(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L1 (bright)</td>
<td>100.6</td>
<td>104.7</td>
<td>HgO</td>
</tr>
<tr>
<td>L2 (medium)</td>
<td>100.2</td>
<td>104.3</td>
<td>Ag-Hg alloy</td>
</tr>
<tr>
<td>L3 (dark)</td>
<td>100.2</td>
<td>104.3</td>
<td>~55% Ag-Hg alloy</td>
</tr>
<tr>
<td></td>
<td>100.9</td>
<td>104.5</td>
<td>~45% HgO</td>
</tr>
</tbody>
</table>

In Figure 3-11, the most probable explanation for the excitation at 100.6 eV is a Ag-Hg interaction with the possibility of HgO on the surface [29,30]; this is supported by the noticeable broadening of the 4f\textsubscript{7/2} peak. While their structural phase(s) is still unclear, Ag-Hg image particles have been previously reported by Barger and White [31], Swan et al. [32], and Ravines et al. [19]. The fact that Hg(0) is not explicitly observed as a dominant peak is due to the presence of surface oxide and corresponds with the greatest density of oxide residing in high particle (Ag-Hg) density regions [31]. The formation of HgO may have occurred during the exposure of the plate to Hg vapour in the development step or from environmental contamination. From the depth profiles in Figure 3-10, O is present in all areas.

Fine scan spectra for Ag and Au were also collected and are similar to those reported by Kim and Winograd [34] and Bzowski et al. [35] and are consistent with the formation of an alloy in the near surface. This, along with the persistence of Au in the depth profiles (Figure 3-10) suggests that Au is present in an Au-Ag alloy and that the composition of the alloy remains uniform in the near surface volume. The laboratory-based Valence Band (VB) spectra were recorded from regions L1 and L2 and confirms this notion.
3.4.2 Synchrotron-Based XPS Results

The HE-XPS survey spectra (Figure 3-12) were collected at 3.0 keV and 8.0 keV. Based on the density of pure Ag, the estimated analysis escape depth is approximately 3 and 6 nm for 3.0 keV and 8.0 keV, respectively, compared to the first few nanometers for the laboratory excitation source of 1.4 keV [10]. Characteristic core level peaks for metallic Ag (3d), Au (4f), and Hg (4f) were observed. It should be noted that the absorption cross-section and the photoionization cross-section drops by one order of magnitude going from 3.0 keV to 8.0 keV. Fortunately, the drop is comparable in both cases, enabling semi-quantitative evaluations to be conducted [36].

Comparison of the spectrum at 3.0 keV to that at 8.0 keV allows the surface and bulk element distribution to be distinguished non-destructively. The data reveals the presence of Hg near the surface (inset of Figure 3-12) in good accord with the depth profile results from the lab XPS.

![Graph](image)

Figure 3-12 Comparison of region S2 (dark) at 3.0 keV (surface) and 8.0 keV (bulk).
A variation in the Ag-Au ratio (Table 3-5) indicates an increase in an Au concentration with depth; this is in part contributed by the increasing kinetic energy of the Au 4f electrons and the penetration depth of the photon through a homogeneous region of Ag-Au alloys. These results correspond to the Au depth profiles in Figure 3-10 as Au plateaus before reaching its max at 486, 378 and 540 nm for regions L1-3, respectively. Comparing the Au 4f\(_{7/2}\)/Ag 3d\(_{5/2}\) ratio within the highlight and the midtone regions, an increase of \(\sim 75\%\) and \(\sim 80\%\) in the Au/Ag ratio for the highlight and midtone region, respectively, is observed with increasing depth (i.e., from 1.4 to 8.0 keV). This slightly smaller degree of Au presence in the highlight region may suggest that the small particles constrain the diffusion process. While in the midtone region, the relative decrease in image particle density facilitates a greater degree of diffusion while maintaining the Au signal on the surface from the image particles.

| Table 3-5 Ratio of Au 4f\(_{7/2}\)/Ag 3d\(_{5/2}\) within a highlight region (S3) and a midtone region (S4) at all three energies: 1.4 keV, 3.0 keV, and 8.0 keV. |
|-----------------|-----------------|-----------------|
|                 | Lab XPS (1.4 keV) | HE-XPS (3.0 keV) | HE-XPS (8.0 keV) |
| S3 (highlight)  | 0.135           | 0.166           | 0.248           |
| S4 (midtone)    | 0.115           | 0.156           | 0.226           |

The VB from the HE-XPS (Figure 3-13) shows Hg peaks at 8.2 ± 0.2 eV and 10.9 ± 0.1 eV, a spin-orbit doublet of the 5d\(_{5/2}\) and 5d\(_{3/2}\) orbitals, respectively [37]. The intensity of this feature is greatest in area S3 (bright) and weakest in S2 (dark) on the test plate. This suggests that the relatively greatest amount of Hg resides in the bright regions (i.e., areas of high image particle density). Previous work has shown that at relatively lower temperatures (such as those used in the daguerreotype production process) the interaction between Hg and Ag is weak [37]. The VB results suggest that the Hg 5d band exhibits little hybridization with either Au or Ag, contradicting the understanding that the image particle is comprised of an Ag-Hg amalgam [32]. However, further work should be pursued (possibly with X-ray emission spectroscopy) to confirm this finding.
Figure 3-13 HE-XPS VB collected at 3.0 keV from the daguerreotype test plate at all four regions: S1 - bright medium, S2 - dark, S3 - bright, and S4 - medium. The bandwidth and apparent 5d spin-orbit splitting is shown.

The VB is sensitive to the alloying of Ag-Au, which varies with depth in this sample. The Ag-Au alloy is confirmed by the apparent spin-orbit splitting, shown in equation 3-1 and is observed in the VB (Figure 3-13) [38].

\[ \Delta_{obs} = \sqrt{\Delta_{s}^2 + \Delta_{5d}^2} \]  

(3-1)

The literature suggests the transition from pure Au to dilute Ag-Au corresponds with the narrowing of the d-band and apparent spin-orbit splitting [35]. The Au 5d bandwidth (\(\Delta_{5d}\)) is very sensitive to the number of surrounding Au neighbor atoms; this band term decreases with the number of nearest neighbours [38].

Using the calculation method from Henke et al. [39], the band term was calculated for regions S1 – S4 as 1.842 eV, 1.837 eV, 1.842 eV, and 1.952 eV, respectively. Pure Au metal has an apparent 5d splitting of 2.72 eV that reduces upon dilution into the Ag-Au form and, in some instances, can approach Au’s atomic value of 1.52 eV [35]. As the
number of peripheral Au atoms decreases, the $\Delta_{5d}$ value decreases. Therefore, as S4 (midtone) has the highest $\Delta_{5d}$ parameter the greatest amount of Au-Au interaction occurs in this region, indicating a slightly Au-rich alloy compared to other regions. Correspondingly, the other regions have a reduced $\Delta_{5d}$ parameter and are relatively consistent with one another, indicating uniformity.

### 3.5 Conclusions

Synchrotron-based analysis, both from XANES and XPS, proved to be a valuable technique to the study of daguerreotypes; no physical or chemical variation was observed on the surface after exposure to X-rays. Moreover, this study provides information pertinent to the advancement of the chemical understanding to both contemporary and historic plates.

Firstly, the Ag $L_3$-edge showed that the image particles on the surface form an alloy with a fcc structure and that the degree of Au diffusion into the Ag plate differed across the surface, which was confirmed by examining the Au $L_3$-edge and through the use of both laboratory-based and HE-XPS sources. Depth profiles from laboratory XPS provided evidence of the formation of Au-Ag alloys and were confirmed by HE-XPS Au 4f$_{7/2}$/Ag 3d$_{5/2}$ ratios at 3.0 and 8.0 keV.

Secondly, while the Au $L_3$-edge revealed the shadow region (A1) to have the greatest degree of Ag-Au alloying, the highlight region (A3) possessed the greatest Au surface concentration and variation in alloys composition, confirming that the relative amount of Au in the Ag-Au alloy varies between different tonal regions on the daguerreotype surface. As estimated from the Au XANES analysis, an average alloy composition of Ag$_{90}$Au$_{10}$ was determined for the shadow and midtone regions while the highlight region suggested an average alloy composition of Ag$_{73}$Au$_{27}$. This variation in the Ag-Au alloy across bright to shadow regions should be considered before conservation treatments are applied as each region of the plate will react differently to the proposed method. While the variations of the AgAu alloy may not result in a linear trend from shadow, midtone, and highlight regions (due to how the plate was prepared that would impact the amount of total Au on the plate, how the plate has aged, and the range of grey tones available for
study), it is possible that the sensitivity of the analysis and fitting method is not good enough to show a greater difference between the various regions. However, future work could include the use Ag/Au ratios from XRF data for a more direct analysis.

Thirdly, examination of the Hg L\textsubscript{3}-edge suggests that metallic Hg was present on the surface but amalgamation with the Ag image particles was not obvious. This was confirmed by the HE-XPS analysis and suggests that the Ag-Hg alloy is not as substantial as previously reported. Both lab and SR sourced XPS showed Hg was present only within the first 1-2 nm of the surface and that alloying with Ag was possible but not consistent across all regions. Due to the inherent variability between plates, it is challenging to assert a set of Ag-Hg at. % values that would apply to all daguerreotypes. Importantly, if Hg is not integrated in the image particle amalgam, this may prove hazardous when conservation efforts are performed (i.e., Hg may be unknowingly removed during the cleaning process).

Finally, the S K-edge revealed the presence of sulfates and sulfides on the surface, in the form of Ag\textsubscript{2}S and Ag\textsubscript{2}SO\textsubscript{4}, respectively. Data may suggest the presence of Ag\textsubscript{2}S-nanoparticle interactions in brighter regions as well as organic sulfonate species across all regions of the sample. Organic S may be residue from the final wash step in the test plate’s production. Environmentally sourced S is most likely the primary source of chemical deterioration on the daguerreotype surface.

### 3.6 References


Chapter 4

I was taught that the way of progress was neither swift nor easy.

Marie Curie, physicist (1867 – 1934)

4 Analysis of 19\textsuperscript{th} Century Daguerreotypes with Synchrotron Light: a XRF and µ-XANES Analysis

4.1 Introduction

In Chapter 3, SR was established as a safe and effective method for examining the daguerreotype surface. In this chapter, two 19\textsuperscript{th} century daguerreotypes, supplied by the NGC, were examined with SR-based XRF and XANES; SEM-EDX was also used. These complementary techniques were used to study the surface morphology, element distribution, and variation in chemistry across the surface of the historic plates with special attention on tarnished regions. Three objectives are the focus of this chapter: 1) to examine various forms of surface corrosion found on daguerreotypes in order to determine their composition, distribution, and origin; 2) to investigate how tarnish impacts the image particles and thus the image itself as well as how the tarnish accumulates across high detail regions; 3) to assist in establishing effective cleaning methods from the information obtained in objectives 1 and 2.

* A version of this chapter has been published in *Herit. Sci.* \textbf{2018}, 6 and *J. Synchrotron Rad.* \textbf{2019}, 26.
4.2 Materials and Methods

4.2.1 Sample Selection and Preparation

The NGC (Ottawa, Canada) provided the two 19th century daguerreotypes examined in this chapter (Figure 4-1). These plates were chosen as they demonstrate a number of features that are characteristic of daguerreotype tarnish (i.e., fogging, corrosion around the perimeter, discolouration, discontinuous deterioration products, etc.). Once produced, each plate would have been mounted between a brass mat and a cover glass, which were bound together with a paper tape and an adhesive. This assembly was then placed within a small case of leather and wood. It is not known if any previous conservation treatments were used prior to being received by the NGC; no treatment or cleaning was conducted by the NGC prior to SR examination. The plates were examined without any preparation.

Figure 4-1 Daguerreotypes of an (A) unidentified woman (accession number SC1) (B) and an unidentified man and woman (accession number PSC70:112) both from the National Gallery of Canada, ca. 1850s.
Each plate was examined visually with optical microscopy and regions of interest (ROIs) were identified. Various forms of degradation were selected and examined with SEM-EDX, XRF and micro-XANES (µ-XANES). Along with degradation regions, the eye region was also selected as it contains a range of grey tones, typical of daguerreotypes, within a relatively small area and thereby can provide insight into how degradation products accumulate and disseminate across varying image particle density regions. One proposed cause for degradation that will be discussed is the deterioration of the cover glass. While the original cover glass was not available for analysis, there is ample documentation in the literature regarding the physical and optical qualities of glass degradation features relevant to the tarnish regions analyzed in this study.

4.2.2 X-ray Absorption Near Edge Structure

The SXRMB (06B1-1) line of the CLS was used to collect the XANES spectra from each daguerreotype. Each daguerreotype was secured to the sample holder using alligator clips; strips of weighing paper were placed between the clip and the daguerreotype to prevent scratching of the surface. The beam was monochromatized by a Si(111) double crystal monochromator; Ag, Cl, and S XANES were collected in FLY mode with a spot size of 10 × 10 μm². The Ag L₃-edge XANES was collected with a 2.00 eV step size below, 0.15 eV step size at, and 0.75 eV step size above the edge. The Cl K-edge XANES was collected with the same set of parameters. The S K-edge was collected with a 2.00 eV steps below, 0.20 eV step at, and a 0.75 eV step above the edge. XANES spectra were compared to standards listed in Table 4-1. The standards used in this study, aside from the Ag-Au alloys (presented in at. %), were obtained through Sigma-Aldrich. The production of the Au-Ag alloys is reported elsewhere [1]. The number of scans collected for the XANES analysis of the daguerreotypes depended on the intensity and signal to noise ratio of the signal but ranged between 2 and 5. This varied between locations within and between the two plates.
Table 4-1 List of standards used for XANES analysis.

<table>
<thead>
<tr>
<th>Element of Interest</th>
<th>Standard(s) Examined</th>
<th>Edge Jump Analyzed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>Ag, Ag₉₅Au₅, Ag₇₅Au₂₅, AgI, AgCl, AgBr, Ag₂O, Ag₂S, AgNO₃</td>
<td>L₃-edge</td>
</tr>
<tr>
<td>Cl</td>
<td>AgCl, NaCl, KCl, HgCl₂, HAuCl₄, AuCl₃</td>
<td>K-edge</td>
</tr>
<tr>
<td>S</td>
<td>Ag₂S, Na₂SO₄, Na₂SO₃, CuS, Cu₂S, HgSO₄, HgS</td>
<td>K-edge</td>
</tr>
<tr>
<td></td>
<td>Na₂S₂O₃•5H₂O, Au₂S, Au₂SO₄</td>
<td></td>
</tr>
</tbody>
</table>

4.2.3 X-ray Fluorescence

The medium energy X-ray microprobe end station, SXRMB (06B1-1), was also used to collect the XRF images [2]. A Si(111) double crystal monochromator and KB micro-focusing mirrors achieved a beamsize of ~10 μm. The XRF maps were obtained with PFY of Ag Lα and S and Cl Kα X-ray emission; scan parameters presented within this chapter are summarized in Table 4-2. XRF images for Ag, Cl, and S are the focus of this study. The spot size of the beam at the specimen was ~10 μm × 10 μm at an incident energy of 3950 eV, which is above the Ag L₃,2-edge (3351 eV and 3524 eV, respectively), the S K-edge (2472 eV), and the Cl K-edge (2822 eV).
Table 4-2 Scanning parameters for the daguerreotype SR-XRF maps.

<table>
<thead>
<tr>
<th>Figure</th>
<th>Incident Energy (eV)</th>
<th>Pixel Size (µm)</th>
<th>Dwell Time (sec)</th>
<th>Scan Size (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 4-8</td>
<td></td>
<td>15 × 15</td>
<td></td>
<td>1600 × 1000</td>
</tr>
<tr>
<td>Figure 4-9</td>
<td>3 950</td>
<td>40 × 40</td>
<td></td>
<td>2000 × 1200</td>
</tr>
<tr>
<td>Figure 4-10</td>
<td></td>
<td>10 × 10</td>
<td>1.0</td>
<td>600 × 550</td>
</tr>
<tr>
<td>Figure 4-11</td>
<td></td>
<td>25 × 25</td>
<td></td>
<td>2625 × 1615</td>
</tr>
<tr>
<td>Figure 4-12</td>
<td></td>
<td>25 × 25</td>
<td></td>
<td>2035 × 1310</td>
</tr>
</tbody>
</table>

4.2.4 Synchrotron Data Processing

All XANES spectra were analyzed using an Athena software package [3]. After background subtraction, normalization (edge jump normalized to unity), and spectrum averaging, all spectra were calibrated, following the procedure outlined by Ravel [4]. When appropriate, LCF analyses were performed on normalized spectra. As such, an LCF models a spectrum of unknown composition using a series of known reference spectra, the number of which depends on the complexity of the unknown system. Each standard spectrum is interpolated onto the energy grid of the unknown spectrum. Goodness of fit is estimated by taking the difference between the collected spectrum and the fitted spectrum. The LCF analysis should be taken as semi-quantitative at best, since non-uniform distribution of substances and varying penetration depth of the photon will contribute to the uncertainty of the fit as well as the energy calibration. All fits are presented in Appendix F.

XRF maps were created using the PFY of the element of interest (i.e., Ag Lα (2984 eV), S Kα (2307 eV), and Cl Kα (2622 eV) X-ray emissions, for Ag, S, and Cl map respectively) normalized to I₀ (the intensity of the exciting X-ray), and analyzed using the SMAK software program [5].
4.2.5 Scanning Electron Microscopy Energy Dispersive X-ray

Scanning electron microscopy images from both daguerreotype plates were examined with the LEO (Zeiss) 1540XB FIB/SEM instrument at the Western Nanofabrication Facility. Topographic imaging was performed at 1 kV with a working distance of 4 mm and backscatter imaging at 10 kV and 9 mm. The Oxford instrument X max 50 detector was used for EDX spectroscopy and analysis was performed with INCA analysis software [6].

4.2.6 Optical Microscopy

Optical microfocus images and feature profiles of specific tarnish features were acquired using a Leica DVM6 digital optical microscope with Leica Application Suite X processing software within the Department of Chemistry at The University of Western Ontario.

4.3 Results and Discussion

4.3.1 Surface Morphology of the Daguerreotype Surface

The study daguerreotype (SC1) (Figure 4-1A) showed patches of white haze across the majority of the portrait, entirely masking the woman’s body. This type of haze, typical for tarnished daguerreotypes, has been previously attributed to AgCl [7]. Under this photolytic tarnish, the characteristic image particles of each region can be seen with SEM (Figure 4-2). The particles are small and densely packed in the highlight region and sparsely dispersed and inconsistently shaped for the dark region (Figure 4-2). The presence of the larger image particles confirms that the woman’s shoulder has a dark appearance, despite the white haze that masks the image. While some smaller particles were observed, which are not expected in the shadow region, in the shadow region they may be the result of the photo-catalyzed reaction of AgX (where X = Cl\(^-\), Br\(^-\), or I\(^-\) bind to Ag particles) or a part of the tarnish layer, not the image particles. The majority of the particles within this region correspond in size to the reported values, 0.1 – 1 µm and 0.25 – 2.5 µm for highlight and midtone regions, respectively and 10 – 50 µm for dark areas [8].
Figure 4-2 SEM images from daguerreotype SC1 (Figure 4-1A) of both a highlight region (top) and shadow region (bottom).

A variety of tarnish defects (Figure 4-3) are observed on plate SC1 (Figure 4-1A) including flattened dark circles, white fogging across broad regions of the image, bubbles, and protruding crystalline particles. The presence of red and blue tones suggests the presence of Cu$_2$O, Ag$_2$O, and Ag$_2$S and/or silver-gold-sulfide compounds (such as AuAgS or AuAg$_3$S$_2$) on the surface, respectively [8-10]. The majority of this coloured tarnish is observed along the perimeter of the plate, suggesting that it may have originated from the contact between the daguerreotype and the metal frame.
Figure 4-3 Optical microscope images showing the variety of tarnish features found on the surface of SC1 (Figure 4-1A).

Figure 4-4 shows an SEM electron image and accompanying EDX images of a tarnished spot on plate SC1 (Figure 4-1A), whose center presents a crystalline, dendrite-like structure. These branches, which fold outwards, are rich in K and Cl. Enrichment of C is seen at the base and P is present in hot spots at the edges of the dendrite features. Oxygen is observed to be associated with the P, consistent with the presence of a phosphate. The K on the surface may arise from the deterioration of the cover glass under which the daguerreotype was enclosed [11,12]. Dendrite-like structures containing K and P have been previously observed with SEM as a result of leaching from a cover glass that was originally designed to protect the daguerreotype from corrosion [13]. Furthermore, dendrites have previously been observed in non-uniform corrosion on Ag surfaces [14]. Another possible source for K is the production process; Humphrey [15] discusses various uses of K within the 19th century daguerreotype process. For example, dilute potassium cyanide was used to increase the “brilliancy of the daguerreotype” after the
gilding step [16]. The photosensitising step may also be the source for residual Cl, which was observed with EDX. The presence of Cl on the daguerreian surface has also been attributed to glass deterioration [16]. Although K and Cl are common components of historic glass, as the cover glass was unavailable for a comparative analysis, their origin remains unknown.

Figure 4-4 SEM electron image from plate SC1 (Figure 4-1A) with accompanying EDX elemental maps of a tarnish spot. Maximum elemental concentration represented with greatest colour intensity with minimum concentration illustrated by black within each image.

A region of the woman’s eye in daguerreotype PSC70:112 (Figure 4-1B) was also examined with SEM; the specific ROI is indicated in Figure 4-5. SEM images of the particle distribution between the highlight and shadow regions are shown in Figure 4-6 with examples of the size, shape, and distribution typical of a tarnished highlight and a shadow region provided in Figure 4-6A-C. The boundary between these two regions is shown with a dashed line in Figure 4-6D. Typical of the tarnished daguerreotype surface, a rough corrosion layer is observed across the surface. Elemental maps (Figure 4-7) were obtained from the border of the blemish region (note EDX label in Figure 4-6A); Cu, C, S, Cl, and O were detected. The C and O are indicative of organic contamination while
the Cu may be assigned to either cover glass deterioration or diffusion from the underlying plate through grain boundaries and/or at edges of the daguerreotype [17] though this diffusion mechanism has been questioned [10]. Thinning of the Ag overlayer during the original production of the daguerreotype plate (i.e., during either the cold welding process or from the polishing step) cannot be excluded.

Figure 4-5 SEM electron image of the woman’s eye on daguerreotype PSC 70:112 (Figure 4-1B) with SEM region of interest (ROI) indicated.

Figure 4-6 SEM images from PSC 70:112 (Figure 4-1B) collected from within ROI region indicated in Figure 4-5. (A) Example of a tarnished shadow region; EDX ROI that is shown in Figure 4-7 (B) high magnification of shadow region (C) high magnification of highlight area (D) transition between highlight and shadow regions.
Figure 4-7 SEM-EDX Ka₁ line images for Cu, C, S, Cl, and O from tarnished surface of daguerreotype PSC70:112 (Figure 4-1B). Brightest colour intensity indicates the relative concentration maximum for each element and black correlates to the relative minimum elemental concentration.

4.3.2 Synchrotron XRF and μ-XANES Analysis

X-ray fluorescence images (Ag, Cl, and S) and accompanying μ-XANES spectra of a tarnish spot found on the side of the woman’s face in daguerreotype SC1 (Figure 4-1A) is shown in Figure 4-8. Due to the relatively shallow penetration depth at the incident energy of 3950 eV, tonal variations can be seen in the Ag XRF map (i.e., regions of low image particle density correlate with the greatest Ag fluorescence signal). The relative decrease in Ag intensity at the center of the tarnish spot correlates to an increase in Cl and S signal. The Cl XRF image does not follow the elemental distribution found in Ag and S. The greatest intensity of Cl was found at the center of the blemish with a lower, essentially uniform distribution, observed throughout the rest of the image, which corresponds to the haze observed in the optical images.

The Ag L₃-edge (Figure 4-8), which arises from the excitation of a 2p₃/₂ electron to unoccupied bands above the Fermi level, displays no sharp peak at the edge (3351 eV) indicating a full Ag d band. The subsequent oscillations are indicative of a fcc structure of Ag metal [1,18]. Spectra 1, 2, and 3 show little variation and most closely resemble the Ag standard, consistent with the results presented in Chapter 3.
The Cl K-edge (Figure 4-8) represents the excitation of an electron from a 1s orbital to a previously unoccupied 3p orbital. The majority of the signal within the blemish (spectrum Cl 1) originates from NaCl, an observation confirmed by the μ-XANES standard. This is corroborated with the LCF analysis. The presence of NaCl at the center of the tarnish spot could be a result of Na⁺ precipitation from the cover glass onto the daguerreian surface via an ion-exchange reaction by hydrogen ions (equation 4-1), resulting [11,19,20].

\[-\text{SiO-Na}^+ + \text{H}_2\text{O} \rightarrow -\text{SiOH}^- + \text{Na}^+ + \text{OH}^-\]  

Spectrum Cl 2, which was taken outside of the blemish spot in the white haze, matches that of the AgCl standard, corroborating previous findings [7].

Only one location (spectrum S 1) for the S K-edge XANES is reported (Figure 4-8), as the counts were too low to collect a spectrum in other regions of the map. The primary
inflection point for the absorption spectrum collected at the blemish center occurs at 2487.2 eV with a post edge absorption feature at 2499.2 eV. When compared to the S standards, LCF analysis, and the characteristic resonance at ~2487 eV, the principal contribution is solely from \( \text{SO}_4^{2-} \) [21]. The presence of sulfate ions may be the result of cover glass deterioration as sulfate complexes have been established as a common degradation product [13].

Given the contained environment in which the daguerreotype would have been held, there was most likely an active and ongoing exchange between the daguerreotype surface and the cover glass. Although environmental contamination should also be considered [8], the effects of such contaminants are expected to be minimal while the plate is contained in its casing. However, as plate SC1 (Figure 4-1A) was removed from its case for an unknown period of time (prior to being acquired by the NGC), exposure to the environment may play a larger role in the degradation of the surface. Any contamination from indoor air would depend both on S and Cl concentrations in the air and the length of exposure. Long exposure to low concentrations of S and Cl might be expected to generate the effects observed in this report. Examples of typical indoor (i.e., museums) concentrations include \( \text{H}_2\text{S} \) (0.3 ppb), \( \text{COS} \) (0.6 ppb), \( \text{SO}_2 \) (30 ppb), \( \text{HCl} \) (0.4 ppb), and \( \text{Cl}_2 \) (not detected) [22-25] and airborne concentrations to be 4 ng m\(^{-3}\) for \( \text{Cl}^- \) and 720 ng m\(^{-3}\) for \( \text{SO}_4^{2-} \) [26]. These values should be considered as representative concentrations and will vary depending on the environment.

Bubbles were observed at multiple locations on the daguerreotype; one example is shown in Figure 4-9. This location shows a cluster of bubbles that are enclosed by a darkened circular band. Small image particles are observed above the discoloured circle, suggesting the presence of a precipitate. Although conservators have informally noted bubbles on the daguerreian surface and have attributed their presence as a product of “weeping glass” [8,13,15], they have not been discussed in depth in the literature. While there is no direct notion of cover glass corrosion leading to these particular surface features on the daguerreotype surface, sticky droplets on the inner surface of daguerreotype cover glasses are often observed [8,13] but cannot be confirmed in this case as the cover glass was not examined. SR-XRF revealed the bubble to be primarily
composed of Cl and S, with hotspots of S observed outside of the bubble, where the precipitate products were noted in the optical image (Figure 4-9). The S XRF also shows a concentrated band that inversely correlates to a band in the Ag XRF map.

![Diagram of XRF and XANES spectra](image)

**Figure 4-9 SR-based XRF and µ-XANES collected from a bubble observed on daguerreotype SC1 (Figure 4-1A).**

The Ag L₃-edge XANES shows similar results to those in Figure 4-8, where the majority of the signal is impacted by the Ag substrate. As metallic Ag has a full d band, no sharp peak (the WL) is observed. In contrast, metals with partially filled d bands always exhibit an intense resonance at the rising edge [27]. However, when comparing the two Ag L₃-edge spectra to the Ag standard, the absorption bands in the experimental spectra are weaker (Ag 1 and Ag 2) than in the Ag standard, a result of s-d hybridization. This confirms the presence of an Ag-Au alloy, a result of the gilding process.

The Cl K-edge XANES (Figure 4-9), with a threshold located at 2822 eV, was collected at a hotpot found within the bubble (spectrum Cl 1). While AgCl is often the primary Cl tarnish feature noted in literature [7], at this location it only accounts for 2.4 wt. % of the
signal (determined from LCF). The major contributor to the Cl K-edge spectrum is from KCl, which was estimated to be 97.6 wt. %, of the experimental spectrum. Similar to the tarnish feature discussed in Figure 4-8, this may be another example of ion migration, in this case K\(^+\), from the corroding cover glass that is subsequently deposited on the daguerreian surface [28].

The S K-edge is composed of two major composite peaks at approximately 2472.5 eV and ~2482 eV (Figure 4-9), the first of which arises from a 1s to 3p transition. This differs from the S K-edge spectra that are shown in Figure 4-8 and Figure 4-10 (see below). This may be due to the presence of CuS, which was determined to make up 43.4 wt. % of the experimental spectrum with LCF analysis, with SO\(_4\)^{2-} (6+) and S\(^2\) (2-) making up the remaining 6.7 and 49.9 wt. %, respectively. Crystalline Cu salts have been reported on the surface of daguerreotypes [16,29] and the accretion of Cu salts has been noted by Barger and White [8] as a result of cover glass deterioration. Other studies have also reported that glass corrosion can produce copper oxides and copper sulfides [29,30]. Another possibility for the presence of Cu on the surface may be the result of Cu diffusing through grain boundaries and/or holes in the Ag, as Marquis et al. [29] have previously noted.

The tarnish spot located above the woman’s head on daguerreotype SC1 (Figure 4-1A) shows a central, flat blemish encircled by a green ring, followed by a yellow halo (Figure 4-10). The entire feature is surrounded by blue tinted ring (optical image supplied in Figure 4-3; top center). A precipitate is observed on the surrounding ring. The Ag XRF map reveals an even distribution of Ag across the image except for a sharp decrease in concentration at the center of the tarnish feature as well as a slight decrease in intensity where the blue band encircles the blemish. The Cl XRF image shows the center of the blemish has the greatest amount of Cl with a slight increase in concentration of Cl along the exterior. Similar concentrations of S are observed in the outer-most ring of the feature that correlates with the visibly darker degradation products seen in the optical image, attributed to S accumulation [31].
Figure 4-10 SR-based XRF and µ-XANES from a tarnished spot on daguerreotype SC1 (Figure 4-1A).

Similar to the Ag L₃-edge XANES collected at the other tarnish locations (Figure 4-8 and Figure 4-9), the absorption regions Ag 1 and Ag 2 indicate the dominance of the Ag substrate. The decreased area under the curve, when compared to the Ag standard, indicates a small concentration of Au alloyed with Ag [32].

The location of the Cl K-edge jumps (Figure 4-10) in both spectra (Cl 1 and Cl 2) and the subsequent oscillations match those of the AgCl standard. Like the other examined locations, NaCl and KCl were also detected, pointing to cover glass deterioration as a source for the degradation spot. While LCF analysis also noted the presence of HgCl₂, which may be due to residual halide that was trapped in the substrate and subsequently reacted with Hg during plate “fixing”, the reported amounts do not provide substantial evidence.
Only one S K-edge was collected at the center of the blemish due to the low counts of S on the perimeter. The threshold resonance of the S K-edge is due to the transition of a 1s electron to p-like states in the LUMO and LUMO + 1 etc. or to the conduction band (CB). The XANES intensity maximum of the disulfide is almost a factor of 3 less than that of the sulfate (SO$_4^{2-}$) peak [33]; this is not unexpected since p densities of states are depleted when S is highly oxidized [34]. Linear combination fit results indicate the experimental spectrum to be composed of 20.2 wt. % HgSO$_4$, 4.3 wt. % Na$_2$SO$_4$, 58.8 wt. % Ag$_2$S, and 16.8 wt. % thiosulfate. The presence of multiple forms of sulfur points to a complicated degradation process that occurs within the daguerreian system [35,36].

To examine how the tarnish is distributed across varying densities of image particles on the surface, the eye region on both plates was chosen as they contain a range of grey tones that typify daguerreotypes. X-ray fluorescence images of the man’s right eye (Figure 4-1B) are shown in Figure 4-11. Setting the incident energy above the Ag L-edge excites the image particle as well as the bulk of the plate. The production of a detailed image is due to the image particles on the surface and the shallow penetration depth of the soft X-ray. Similar to the previous Ag XRF images collected from tarnish locations, the intensity of the Ag signal inversely corresponds to the distribution of image particles. For example, the iris of the eye, which is represented by dark red on the colour scale, is a region of low image particle density. Conversely, regions of high image particle density such as the highlight of the eye, has a decreased Ag fluorescence signal (~10%). The Ag fluorescence intensity may be impacted by an overlayer of polluting elements (AgCl and/or Ag$_2$S) and/or from an enhanced overlayer of Au, a result of the gilding process. The S XRF map shows a non-uniform distribution of S signal, which is a common morphological characteristic of the sulfidation of Ag [17]. Similarly, the Cl fluorescence signal follows an indistinct, random distribution across the eye region.
Figure 4-11 SR XRF maps from daguerreotype PSC70:112 (Figure 4-1B) of Ag, Cl, and S with corresponding μ-XANES for S and Cl K-edges shown on the right.

The chemical environment was examined with μ-XANES. At all three locations where the S K-edge XANES was collected (Figure 4-11), the primary feature is observed at 2472.5 eV, which arises from a 1s to 3p transition. The location of this first transition suggests a covalent Ag-S interaction [37] and is seen as the double feature of the first peak (emphasized by arrows in spectrum S 1 Figure 4-11), indicating the dominance of Ag₂S at all sites [37]. This was supported with LCF. The second peak at about 2482 eV corresponds to an oxidized form of S where the oscillation is characteristic of multiple scattering [33]. These two observations suggest a mixture of S compounds at the surface.

The Cl K-edge (Figure 4-11), which represents the excitation of an electron from a 1s orbital to a previously unoccupied 3p orbital, has a threshold located at 2822 eV. Examination of the edge jump location and post-edge oscillations, AgCl was the dominant contributor. This aligns with the LCF analysis.
Ag$_2$S and AgCl are the most common forms of Ag corrosion [38,39]. Environmental Cl compounds contribute to the tarnishing of the daguerreotype surface; the rate of tarnish formation will be concentration dependent [40]. Some AgCl on the daguerreotype surface may be residue from the sensitization step (equation 4-2) [41]. Similar to the exposure step, any residual AgCl trapped within the Ag lattice may undergo reduction from UV exposure (equation 4-3) to form Ag nanoparticles [42]. This has been noted to occur on daguerreotypes under natural and experimental conditions [43].

\[
2 \text{Ag}(s) + \text{Cl}_2(g) \rightarrow 2 \text{AgCl}(s) \quad (4-2)
\]

\[
2 \text{AgCl}(s) + h\nu \rightarrow 2 \text{Ag}(s) + \text{Cl}_2(s) \quad (4-3)
\]

As well, deterioration of the cover glass could also lead to the production of AgCl as a result of alkali ions in the cover glass matrix interacting with water vapour [13].

The tarnishing of Ag by S, which commonly produces a non-uniform film, can be attributed to several environmental considerations such as temperature, relative humidity, the amount of reduced sulfides in the atmosphere [44], and state of the Ag surface [45]. Other factors such as the handling of the daguerreotype and perhaps physical disturbance by the owner (i.e., buffing with a cloth), would also impact the degree of corrosion on the surface. The placement of daguerreotypes within a sealed frame not only protects the surface from abrasions but also serves as a buffer from variations in relative humidity; moisture content has been shown to significantly impact the corrosion rate on Ag [44]. However, it is also quite likely that a microclimate is created between the glass and the plate, which may facilitate the degradation of the Ag surface.

Possible sources of S corrosion include H$_2$S, SO$_2$, carbonyl sulfides (OCS) and organic sulfides [26,40,46-48]; H$_2$S have been shown to be a source of Ag$_2$S at concentrations as low as 0.2 parts per billion (ppb) [49,50]. In addition, while organic sulfides are generally present in low concentrations they have been shown to rapidly tarnish Ag surfaces, especially in the presence of light [50].

In urban environments, H$_2$S, SO$_2$, and OCS have the greatest reported concentrations of any likely tarnish sources. However, the reaction between Ag and SO$_2$ is relatively slow
While daguerreotypists were often part of expeditions to remote locations (i.e., the California Gold Rush of 1848 [52]), the majority of daguerreotype studios were found in city centers with their benefactors also residing in these urban environments. Therefore, any S species that would come into contact with the plate, which would occur prior to their placement behind a cover glass, would be from an urban atmospheric environment (for instance H₂S and SO₂) while daguerreotypes produced in nonurban environments would primarily experience OCS [53].

The distribution of Ag, S, and Cl on the woman’s right eye from the study plate was also examined (Figure 4-12). Here, like in Figure 4-11, the Ag XRF shows a relatively greater amount of Ag fluorescence signal from regions with few to no image particles and a relatively lower XRF signal in areas with high image particle density. The details of the eye can also be observed in the S XRF image as the distribution of S follows the location of the image particles. For instance, in the highlight region of the eye, which would appear as a bright/white tone when viewed in normal conditions, a relative increase in S concentration is observed. This suggests that S accumulates in regions of increased surface area. A light outline of the eye is noted in the Cl XRF image but not with the same degree of clarity as in the Ag or S maps.

Absorption spectra for each element were collected at different regions within the eye. The Ag L₃-edge XANES (edge jump located at 3351 eV) represents the excitation of a 2p₃/₂ electron to unoccupied s-d bands above the Fermi level (Figure 4-12). The lack of a sharp rising edge indicates that the d-band is full, like that of pure Ag. Subsequent oscillations arise from the multiple and single scattering of the photoelectrons by the neighboring atoms. Examination of the highlight region (Figure 4-12, spectrum Ag 1) shows a dominance of Ag₉₅Au₅ and Ag standards, indicating minimal alloying between Au and Ag in the highlight region. LCF analysis of the dark region (spectrum Ag 2) shows Ag₉₅Au₅ and Ag₇₅Au₂₅ as the two major contributors, suggesting a greater degree of alloying in this area (i.e., a shadow location of the eye) and aligning with the Ag L₃-edge analysis discussed in Chapter 3 [54].
Figure 4-12 SR XRF maps for Ag, Cl, and S from plate SC1 (Figure 4-1A). Accompanying µ-XANES spectra for each element are shown below their respective XRF image. Cl 1 and Ag 1 are collected from the same area and Cl 2, Ag 2, and S 2 are taken at the same location.

While some information regarding the degree of alloying between Ag and Au can be extracted from the Ag L₃-edge, the findings are minimal as Ag makes up the bulk of the substrate as well as the image particles on the surface. In Chapter 3, analysis of the Au L₃-edge estimated the composition of the Ag-Au alloy in the shadow and midtone regions to be Ag₉₀Au₁₀ while in the highlight regions it was estimated to be Ag₇₃Au₂₇ [54]. An increase in Au in the highlight region is most likely the result of the increased surface area in the high particle density zones while the shadow areas contain a relatively lower image particle density and corresponds to the decrease in relative Au concentration. As Au is primarily associated with the image particles, while Ag is associated with both the image particles and the substrate, an improved accuracy of the Ag-Au alloy composition
can be established when examining the Au L₃-edge. It also explains why the alloy compositions vary between the Ag and Au L₃-edge data. Moreover, deviation from these proposed weight percent values between plates may be due to differing methodologies in the gilding process including but not limited to the composition of the gilding solution, the length of time the solution remained on the daguerreotype surface, the temperature of the heat source placed below the plate, and the composition of the plate itself. Alloying with Au would also impact the probability and possible processes of corrosion. Despite Au’s inert characteristics, when present in a Ag-Au alloy with a Au content less than 50%, Au’s corrosion and tarnish resistance is greatly reduced [55]. This low concentration of Au in the Ag-Au alloy, the number of phases present, and the microstructure of the alloy will impact the corrosion susceptibility of a material [55].

The Cl K-edge was collected at three different locations (Figure 4-12). Spectrum Cl 1 is associated with the white of the eye (like Ag 1), spectrum Cl 2 corresponds with the iris (like Ag 2), and spectrum Cl 3 represents a midtone region collected at the inner portion of the eye. For all locations, the location of the edge jump (2822 eV) and the subsequent oscillations match the AgCl reference and is consistent with LCF analysis.

Two S K-edge spectra were collected from a highlight (S 1) and shadow (S 2) region. Similar to the previous S K-edge examination, the presence of both sulfide and sulfate compounds was observed. While LCF analysis suggests the presence of Hg and Au bonded to an oxidized sulfur species, it is most likely that a variety of sulfate compounds are present.

An example of the LCF used to semi-quantitatively analyze all XANES spectra is shown for each absorption edge in Figure 4-12 is shown in Figure 4-13. The experimental spectra are shown together with the LCF and difference (Diff.) spectra. This does not provide a quantitative error measurement but is indicative of the goodness-of-fit for the unique model applied to each experimental spectrum.

While previous studies have used artificially tarnished samples to characterize degradation products on the daguerreotype surface, these models are not necessarily representative of natural tarnishing layers [29,56,57]. Moreover, artificial aging in natural
environmental conditions often produce inconsistent results that cannot be quantified [9]. For instance, morphology, microstructure and composition of the corrosion may depend on the artificial corrosion method used. Furthermore, it is not possible to assume that natural occurring deterioration can be explained as a single corrosion state; multiple natural corrosion states must be considered.

![Figure 4-13 (A) Ag L3-edge (spectrum Ag 1) (B) Cl K-edge (spectrum Cl 1) (C) S K-edge (spectrum S 1) from Figure 4-12 with linear combination fit (LCF) and difference (Diff.) spectra for each absorption edge.](image)

The differing distribution of Cl and S observed on both daguerreotypes may be the result of a variety of factors including, but not limited to: 1) differential exposure to the atmosphere, the concentration of which may vary significantly over time; 2) a large number of different chemically reactive sites that are influenced by particle size and/or distribution as well as surface defects, discontinuous gilding surface, and differing degrees of amalgamation between Hg, Ag, and Au; 3) possible effects of the cover glass and the microclimate that is created between the glass and the plate; 4) incomplete washing of the surface during preparation of the original daguerreotype; 5) previous conservation effort(s) where an insufficient wash post-treatment was performed. It is probable that the reactivity of the daguerreotype surface changes significantly from site to site and is one of the challenging problems associated with the analysis of these historical images.
### 4.4 Conclusions

In this chapter, synchrotron-based XANES and XRF were applied to 19th century daguerreotypes. Two key regions of interest were investigated: 1) tarnish defects at various locations across the plate(s) and 2) the eye region. Similar to the findings in Chapter 3, no visible alteration was noted on either of the plates post analysis, demonstrating that both of these synchrotron techniques and the parameters under which they were performed, did not appear to negatively impact these historic images.

In all instances, the primary tarnish compounds identified by XANES were Ag$_2$S and AgCl, confirmed by both S and Cl K-edge examination; XRF found S and Cl to be associated within high-density image particle regions. These results are in agreement with the SEM-EDX analysis. XRF also showed that the distributions of Ag and S were inversely correlated, confirming a preferential accumulation of S within high-density particle regions. It was also observed with XRF that these two elements show different distribution patterns. This may indicate that Cl and S may undergo different reaction pathways due to the variance of surface reactivity across the plate.

While Ag$_2$S and Ag$_2$SO$_4$ were identified as the primary S degradation products, Hg-S interactions (possibly HgS and HgSO$_4$) were also noted. In Chapter 3, minimal amalgamation of Hg with Ag was observed in both the Hg L$_3$-edge XANES analysis and the HE-XPS examination. The observation of a Hg-S bond may suggest that Hg is actively involved in the formation of tarnish on the daguerreotype surface, more so than previously expected. However, the dominant form of S tarnish observed within this work is associated with the corrosion of Ag.

The evidence of a complex corrosion process is shown clearly with both optical and XRF microscopy. XRF of the eye region showed that tarnish correlates with the image particle density and both optical and XRF imaging noted a variety of deterioration compounds and types of blemishes (i.e., colourful halos, crystalline spots, and bubbles) reside on these historic surfaces. These findings suggest that the corrosion process is a result of multiple factors, including but not limited to, 1) possible cover glass deterioration that subsequently causes complex interactions between the daguerreotype surface and the
glass decomposition products, 2) the original production and washing procedures; 3) the storage environment, handling, and atmospheric conditions, and 3) the possibility of previous conservation efforts. Therefore, a combination of conservation treatments is most likely required when treating daguerreotypes.

Before any conservation is proposed, preservation efforts should be conducted, such as the replacement of the cover glass and any deteriorating portions of the case. This would ensure minimal contact with the artefact while optimizing the safety and storage of the photograph. If treatment is deemed appropriate, the most common method is a chemical wash with a NH$_4$OH solution to remove any remaining halides, which are responsible for the appearance of white fog on the surface. To address the presence of black and blue corrosion, which is due to Ag$_2$S and/or Cu$_2$S and Cu$_2$O and/or CuO, respectively, electrocleaning may be pursued if deemed appropriate. The optimal methodology for this treatment is still under discussion in literature; Chapter 6 discusses the impact of electrocleaning on 19th century plates.

4.5 References


Various Other Processes Employed in Taking Heliographic Impressions; Humphrey: New York, 1858.


Chapter 5

Both the man of science and the man of art live always at the edge of mystery, surrounded by it; both always, as the measure of their creation, have had to do with the harmonization of what is new and what is familiar, with the balance between novelty and synthesis, with the struggle to make partial order in total chaos.

Julius Robert Oppenheimer, physicist (1904 – 1967)

5 Recovery of Degraded-Beyond-Recognition 19th Century Daguerreotypes with Rapid High Dynamic Range Elemental XRF Imaging

5.1 Introduction

The overarching goal of this chapter was to investigate the possibility of imaging complete daguerreotype plates. While the findings presented in Chapter 4 showed that SR could provide information on how the tarnish is distributed across the surface as well as the composition of the tarnish, the limitations of the scan area to regions of ~ 1 × 1 cm only provides a fragmented view of these historic images. Therefore, rapid scanning XRF imaging was pursued at the Cornell High Energy Synchrotron Source. By mapping the Hg distribution with rapid scanning, micro-XRF (µ-XRF) imaging, full portraits, which to the naked eye are obscured entirely by extensive corrosion, can be retrieved in a non-invasive, non-contact, and non-destructive manner. This work furthers the chemical understanding regarding the production of these images and suggests that mercury is retained in the image particles despite surface degradation. Most importantly, µ-XRF imaging provides curators with an image recovery method for degraded daguerreotypes, even if the artifact’s condition is beyond traditional conservation treatments.

*A version of this chapter has been published in Nat. Sci. Reports. 2018, 8.*
5.2 Materials and Methods

5.2.1 Sample Selection and Preparation

The two daguerreotypes analyzed in this study (Figure 5-1) were provided by John McElhone from the NGC (Ottawa, Canada). These two plates were chosen as they display a range of tarnish features typical of historic daguerreotypes and were available for loan. The NGC acquired these two daguerreotypes through casual purchases and donations with the intent that they be used for study purposes. Daguerreotype Figure 5-1A is from the NGC Research Study Collection (accession number SC1) and Figure 5-1B is from the NGC collection (accession number PSC 70:111). John McElhone removed plate PSC 70:111 (Figure 5-1B) from its original cases prior to being received for analysis. Daguerreotype SC1 (Figure 5-1A) was acquired by the NGC with no casing. Both of these images have substantial tarnish on the surface, observed as a white haze that covers the image. No sample preparation was conducted prior to analysis other than preliminary electrocleaning and chemical dipping attempts to plate SC1 (Figure 5-1A).
Figure 5-1 Optical images of 19th century daguerreotype (A) SC1 from the National Gallery of Canada Research Study Collection and (B) PSC 70:111 from the National Gallery of Canada collection. The line down the center of SC1 (A) shows the impact of chemical dipping as the left half of the plate has been cleaned with a 1% NH$_4$OH for 30 minutes. Small circles in the top left and right corners of SC1 (A) is the result of a localized electrocleaning effort.

5.2.2 Preliminary Conservation Treatments

5.2.2.1 Chemical Dip

The chemical dip for plate Figure 5-1A was performed at The University of Western Ontario. A 1% NH$_4$OH solution [1] at room temperature (21 °C) was used for 30 minutes to remove residual halides ($X^- = \text{Cl}^-, \text{Br}^-, \text{I}^-$) that cause plate clouding (equation 5-1).

While the parameters outlined by Robinson and Davis [1] suggests running the NH$_4$OH solution across the surface with a dropper bottle, various museum institutions, such as the National Gallery of Canada, uses a bath method, where the daguerreotype is fully submerged in the NH$_4$OH solution. The bath method was used in this study.

$$\text{AgX(s)} + 2\text{NH}_4\text{OH(aq)} \rightarrow \text{Ag(NH}_3)_2^+(aq) + X^-(aq) + \text{H}_2\text{O(l)} \quad (5-1)$$
Any residual halides would depend on the original production process. The plate was subsequently thoroughly rinsed with deionized water and dried in a stream of dry Ar gas.

5.2.2.2 Preliminary Electrochemical Treatment

Preliminary electrochemical treatments were completed using a 10 mm diameter cell filled with 0.1 M NaNO₃ electrolyte at room temperature (21 °C) [2]. The potential was scanned from the open circuit value down to -1.5 V at a scan rate of 10 mV s⁻¹ over a scan range of 1 V. All potentials were measured and quoted against a silver-silver sulfate (Ag/Ag₂SO₄) reference electrode that has a potential of 0.318 V with respect to the saturated calomel electrode. In this three electrode system, the Ag/Ag₂SO₄ electrode is the reference, a Pt wire serves as the counter electrode, and the daguerreotype acts as the working electrode. The open circuit potential was recorded for 600 s before and after each potentiodynamic sweep. Dark spots on the top right and left hand corners of plate SC1 (Figure 5-1A) show the impact of this preliminary electrocleaning treatment.

5.2.3 Synchrotron Radiation Analysis

5.2.3.1 Cornell High Energy Synchrotron Source

The synchrotron experiments were conducted on the G3 line at CHESS (Cornell University, U.S.A). The incident energy was set to 13 025 eV, above the Hg L₃-edge at 12 284 eV, in order to excite fluorescence from the Hg L emission lines. At this incident energy of 13 025 eV, the energy resolution was ~ 1.4 eV. The incident beam was heavily attenuated to approximately 4 × 10⁸ photons/sec in the focal position to avoid saturating the detector. Incidentally this will also reduce the chance of radiation damage (determined through visible inspection pre and post analysis). The working distance was 2 mm between the detector and the daguerreotype. Micro-XRF spectroscopy elemental maps were collected using the Maia-384 element detector by continuously scanning the sample (called fly-scan mode), while the detector and the beam remain fixed [3,4]. The low-energy cut-off of the detector is limited to approximately 2 keV and the energy resolution of the detector is 280 eV at the Mn Kα line, which allows the separation of Hg (Lα₁: 9988.8 eV) from that of Au (Lα₁: 9713.3 eV).
The daguerreotype was posteriorly secured within a metal frame on two-sided Kapton tape while the corners of the photograph were cradled with non-adhesive Kapton film. A $70 \times 80 \text{ mm}^2$ scan range was analyzed with an estimated dwell time of 4 ms per $25 \times 25 \mu\text{m}$ pixel over a collection time of 8.5 h. The beamsize was $20 \times 30 \mu\text{m}^2$. The flat surface of the daguerreotype afforded optimal conditions for data collection and $\mu$-XRF modeling with respect to the calculation of XRF yields. Elemental concentrations are considered to be semi-quantitative. The elemental maps are shown with the observed counts and the maximum intensity threshold adjusted to best represent the high dynamic range data in a single image. The elements of interest were Ag, Au, Hg, and Cu.

### 5.2.3.2 Data Processing

The synchrotron $\mu$-XRF data was processed using GeoPIXE [4]. Elemental concentration maps were produced using the fundamental parameters dynamic analysis (DA) approach. The sample matrix was approximately modeled with reference to Au foil (density = 19.32 g/cm$^3$). Any deviations between the examined daguerreotypes and this Au reference do not significantly affect the ratios of the elemental concentrations examined within this work. All spectra include lead (Pb) and molybdenum (Mo) fluorescence (which are weak since the excitation energy is below the Mo K and Pb L edges), which are from the beamstop and from inside the Maia detector, respectively [5]. An example of a summed spectrum with the associated fit can be seen in the Figure 5-2 with a deconvoluted spectrum presented in Figure 5-3. Elements of interest are selected for the fit, which then appear as individual peaks (multi-colored lines) under the Maia data (green line) in the deconvoluted spectrum (Figure 5-3).

To acquire the spectrum presented in Figure 5-3, an energy calibration in GeoPIXE was completed. This ensures that all 384 pixels of the Maia detector are reporting each fluorescence peak at the same energies. As mentioned, a Au calibration foil was used to generate the calibration standard for the beam energy used in this experiment. The Au calibration applies the new coefficients required to correct for any offsets in the energy scale (x-axis) to each pixel spectrum. This newly calibrated data can now be summed into a single spectrum.
Figure 5-2 Micro-XRF spectrum for daguerreotype PSC70:111 (Figure 5-1B) that has undergone spectra summation, calibration, and fitting in GeoPIXE. Elements of interest are highlighted. Energy resolution of the detector is 280 eV.

Figure 5-3 (A) An example of spectral decomposition from the XRF spectrum of a 19th century daguerreotype from the National Gallery of Canada (PSC 70:111). The green curve represents the Maia data with the individual fits represented by other colors. (B) An enlarged region that focuses on the energy range 8 – 13 keV. Both spectra include the identification of key elements.
The subsequent fitting process involves repeating all and/or some of the following steps: 1) selecting elements relevant to the sample and their emission lines (i.e., K, L, and M); 2) ensuring that the signal filter is accounted for (in this case 5 mm of air); 3) optimizing the fit of the background and the elastic and Compton scattering peaks; 4) restricting the full width half max (FWHM) of the peak fitting and adjusting the low energy tails. Cycling through this process produces the ideal DA matrix from which the elemental maps are generated. Relative trace element concentrations of Hg and Au were determined by selecting regions of interest (i.e., the collar on a dress for a highlight region versus the hair of an individual for a dark region) from the collected elemental maps. This generated a table of elemental concentration values that were then exported from GeoPIXE.

5.3 Results and Discussion

5.3.1 Optical Examination

Optical imaging of the NGC daguerreotypes revealed a range of degradation (Figure 5-1A and Figure 5-1B). It is apparent, due to the surface tarnish, that the images are barely recognizable (Figure 5-1A) when viewed by eye or are beyond recognition (Figure 5-1B). Figure 5-1B shows weak outlines of the original portrait with the details of the face and setting indiscernible. The daguerreotype in Figure 5-1A has tarnish along the perimeter of the image that contains dark degradation areas with oil-like residue. White fogging obstructs all portrait details. A difference in luster is observed between the right and left side of the image (Figure 5-1A) as the left side of the plate was treated with a 30 minute, 1% NH₄OH chemical dip to remove residual halides.

5.3.2 Rapid Scanning XRF

The images of entire daguerreotype plates were obtained with a rapid scanning Maia detector [6], which is capable of high count rates, exceeding $10^7$ photons/second [5]. The Maia data analysis software does not utilize regions of interest (ROIs) but instead fits a curve to each “electronic window” and to the background signal resultant from scatter. This enables both detection and discrimination of the Hg and Au L fluorescence signals over large scan areas in reasonable times in spite of the very large Cu excitation background signal and the lower energy resolution. The Hg/Au ratio for these samples
averaged over the entire scan area is close to one. This means that any errors in the peak fitting resulting in elemental image cross contamination would be equally evident in both the Hg and Au XRF images. If there was cross contamination, a signal spike in the Hg image of Figure 5-4B on the woman’s ring finger where the Au signal is markedly highest would be observed. As no such signal augmentation is present, the fitting routine is performing properly and no appreciable signal cross contamination is observed. While high count rates are not unique to the Maia detector, the images presented within this study greatly benefited from this feature, along with the Maia's low dwell times and the micro-focused beam size.

Micro-XRF Hg distribution images taken before treatment from the two plates (Figure 5-4B and Figure 5-5B) are shown alongside their optical images. The relative distribution of the other collected elements, which includes Cu, Au, and Ag, can be seen alongside the Hg fluorescence image in Figure 5-4 and Figure 5-5. A difference in luster is observed between the right and left side of the optical image (Figure 5-4A) as the left side of the plate was treated with a 30 minute, 1% NH₄OH chemical dip to remove residual halides.
Figure 5–4 (A) Optical image of plate SC1. Optical image illustrates the effects of the use of chemical cleaning. The left half of the plate has been cleaned with a 1% NH₄OH for 30 minutes. A small circular area produced by preliminary electrocleaning is visible on the optical image in the top left hand corner of the plate. (B–E) µ-XRF images of Hg (Lα), Au (Lα), Ag (Lα), and Cu (Kα), respectively.
Figure 5-5 (A) An optical image of plate PSC 70:111. (B-E) µ-XRF images of the Hg (Lα), Au (Lα), Ag (Lα), and Cu (Kα), respectively.

Relative concentrations have been averaged from five dark regions and five light regions from daguerreotype PSC 70:111 (Figure 5-5); an example of this can be seen in Figure 5-6. In the reported values, Cu, along with Ag, shows the relatively greatest concentration of all collected elements. Silver and Cu all show a decrease in relative concentration in the bright regions, which is due to the slight masking of Au and Hg. Conversely, Au and Hg have an increase in relative concentration in regions where image particle density is relatively greater. A similar observation is noted for daguerreotype SC1. However, the Ag and Cu µ-XRF images do not provide any information regarding the nature of the image but solely for the substrate itself; this is due to the relatively harder incident X-ray, which results in the bulk of the plate being the primary signal. It is only in the Hg, and sometimes in the Au, µ-XRF maps that the original image is observed. This is the result
of the interaction between the heated Hg vapour and the Ag surface during daguerreotype processing that causes the distribution of Hg to follow that of the light exposure, and image particles, on the surface [6-8]. Therefore, the distribution of Hg on the surface represents the original image particle distribution. Although the daguerreotype optical image has been lost, the collection of the Hg L fluorescence allows the complete original image to be reconstructed.

![Micro-X-ray fluorescence image of Hg (Lα₁,₂) from plate PSC 70:111. Locations where elemental concentrations were examined are marked by a green circle. Relative average concentrations were calculated from the counts collected at each of the chosen sites. Five locations were chosen from dark areas (D1 – D5) and from bright regions (L1 – L5). Hg (Lα₁,₂)/Au (Lα₁,₂) ratios are presented in the table on the right.](image)

<table>
<thead>
<tr>
<th>Hg/Au Comparison of Dark and Light Regions</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Dark Regions</strong></td>
</tr>
<tr>
<td>D1</td>
</tr>
<tr>
<td>D2</td>
</tr>
<tr>
<td>D3</td>
</tr>
<tr>
<td>D4</td>
</tr>
<tr>
<td>D5</td>
</tr>
<tr>
<td><strong>Light Regions</strong></td>
</tr>
<tr>
<td>L1</td>
</tr>
<tr>
<td>L2</td>
</tr>
<tr>
<td>L3</td>
</tr>
<tr>
<td>L4</td>
</tr>
<tr>
<td>L5</td>
</tr>
</tbody>
</table>
The ability to view the Hg µ-XRF map despite the decline in optical integrity due to tarnish, suggests that relative Hg concentrations and distribution are preserved despite daguerreotype deterioration. This association of Hg with the original image is attributed to its critical role during daguerreotype production. The durability of Hg on the surface as well as the mechanism through which it amalgamates with the Ag particles is currently under debate in the literature [9,10]. To the best of the authors’ knowledge, there have been no proposed tarnish products involving Hg. However, recent work conducted by our group with synchrotron XANES spectroscopy has revealed the possible presence of mercury chloride and sulfide on the surface (see Chapter 4) [11]. A potential dissociation of Hg with the original image may be caused from the de-alloying of the Ag-Hg amalgam. However, this process would not result in the mobilization of Hg from its original position and the relation between Hg and the image particles would remain the same. Therefore, if de-alloying did occur, the image would still be preserved as Hg would still be associated with the image particles and because the specific chemistry of Hg does not matter for the image to be retained through its fluorescence signal. However, if de-alloying has occurred and a plate undergoes a conservation treatment, the Hg may be dislodged and removed in solution, thereby unknowingly impairing the integrity of both the optical image and its potential recovery via XRF.

One such conservation treatment is chemical dipping, a process that targets any residual halides (X’ = Cl’, Br’, I’) on the surface (equation 5-1), which can cause a white fog that masks the image through the formation of a silver halide (AgX). The µ-XRF images, specifically that of Hg, for daguerreotype SC1 (Figure 5-4B) shows no visual impact from the chemical dipping process that was performed on the plate prior to analysis. No division line is apparent in the Hg µ-XRF distribution image from this chemical dip procedure, indicating that the Hg is not involved in the substitution reaction with the 1% NH₄OH solution. Elemental comparison of Hg and Au was conducted to compare the dipped and non-dipped side (Figure 5-7). When comparing like regions (non-dipped bright to dipped bright regions and non-dipped shadow to dipped shadow regions) across this conservation line no notable variation was apparent in Hg/Au ratios, suggesting that the complexing ability of the weak NH₄OH solution only targets the residual halides, not the elements (Au and Hg) that are integral to the image. However, further analysis should
be conducted examining the same areas before and after NH$_4$OH dipping before definitive conclusions are made. While the NH$_4$OH dip does remove the white haze caused by residual silver halides, the daguerreotype image is far from recovered, highlighting the complexity of both the degradation and conservation techniques necessary for these 19th century artifacts. The impact of two different electrocleaning procedures is discussed in the subsequent section.

<table>
<thead>
<tr>
<th>Hg/Au Comparison of NH$_4$OH Dip and Non-Dipped</th>
<th>Dip (green circle)</th>
<th>Non-Dip (blue circle)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Collar</td>
<td>0.1850</td>
<td>0.1884</td>
</tr>
<tr>
<td>Cheek</td>
<td>0.1695</td>
<td>0.1760</td>
</tr>
<tr>
<td>Forehead</td>
<td>0.1691</td>
<td>0.1983</td>
</tr>
<tr>
<td>Chest</td>
<td>0.1060</td>
<td>0.1146</td>
</tr>
<tr>
<td>Waist</td>
<td>0.08610</td>
<td>0.09607</td>
</tr>
<tr>
<td>Hand</td>
<td>0.1722</td>
<td>0.1980</td>
</tr>
<tr>
<td>Background</td>
<td>0.1744</td>
<td>0.1958</td>
</tr>
</tbody>
</table>

Figure 5-7 Micro-X-ray fluorescence (µ-XRF) image of Hg (L$_{\alpha1,2}$) of plate SC1 collected at CHESS. Locations where elemental concentrations were examined are marked by a green circle for the dipped side and a blue circle for the non-dipped side. Relative average concentrations were calculated from the counts collected at each of the chosen sites. A comparison between Hg/Au values from the chemical dipped and non-dipped sides is included. Not all examined regions are marked.

For this work, the incident beam was heavily attenuated to approximately $4 \times 10^8$ photons/sec in the focal position to avoid saturating the detector due to the Cu substrate. This degree of attenuation suggests that mapping daguerreotypes may be well within reach with a high resolution, non-synchrotron source. An effort to develop a laboratory-
based, portable XRF setup with a high count rate detector such as the Maia for imaging daguerreotypes is being considered for a long-term conservation effort. This would be beneficial for the in situ analysis of extremely fragile daguerreotypes not suitable for transportation to a synchrotron facility. Recently, a Maia Mapper using an Excillum MetalJet D2 microfocus X-ray source has been developed for laboratory-based XRF imaging, which has reported an anticipated focused flux of $1.6 \times 10^9$ photons/sec for a source power of 200 W and a 1.0 mm Al filter [12]. With this flux, it should be possible to image a daguerreotype with a laboratory-based setup. However, we propose that using synchrotron μ-XRF mapping of the Hg L lines to image entirely tarnished daguerreotypes, especially those beyond conservation treatment, provides the best technique to preserve these important images of our history and is far superior to previously proposed methods. While a portable system may increase convenience, it is a challenge to match the scan size, step size, beamsize, dwell time, and the ability to select for an energy just above the Hg L$_3$-edge of a synchrotron. Moreover, effort was recently made to image a daguerreotype by a lab-based synchrotron source. Due to the low concentration of Hg on the surface, the acquisition time necessary to image the plate at a reasonable step size was far too long to be feasible. More work needs to be done to determine if laboratory-based XRF imaging is feasible.

Due to the 25 μm step size, some perceived blurriness may be noted in the μ-XRF images. While the exact resolution of daguerreotypes has not been determined (and would ultimately vary from plate to plate), we estimate that to achieve a clarity comparable to that achieved by the naked eye, the step size would have to approach < 10 μm. It may be the case that the original resolution may only be on the order of 20 μm, the statistical comparison of image resolution between the optical and fluorescence images is beyond the scope of this chapter. However, even fine features such as the folds of the man’s tie and in the detailed carving of the high back chair in Figure 5-5B as well as in the beaded bodice of the seated woman in Figure 5-4B are visible on the Hg fluorescence images.

Davis and coauthors have previously used micro-focused XRF imaging to collect Au and Hg M line fluorescence from 19th century daguerreotypes, producing a chemical
reconstruction of the plates using a Rh source run at 50 kV [13]. A major challenge of \(\mu\)-XRF imaging daguerreotypes is the excitation of Cu fluorescence from the substrate, as it produces an overwhelming background signal, masking the tiny fraction of Hg photons that are measured. The energy separation between the Au and Hg M lines (Au = 2122.9 eV; Hg = 2195.3 eV) is much smaller than that of the L lines (Au L\(\alpha\) = 9713.3 eV; Hg L\(\alpha\) = 9988.8 eV), indicating that these signals can be more easily distinguished and fitted using L emission [14]. Davis and colleagues were able to produce a replicate image from their post-processing technique. However, they were examining daguerreotypes that had hardly any tarnish and nearly every sign of physical damage such as scratches are clearly visible in their XRF images. If their methodology were used in this current study, their mode of imaging would not be possible due to the severity of the corrosion on the daguerreotypes analyzed in this study (Figure 5-5A). For instance, factoring in all the differences in scan size, step size, dwell time etc., the scans presented in this work is over 60 000 times faster than that proposed by Davis. The ability to produce a \(\mu\)-XRF scan with excellent clarity in a timely manner is a fundamental advancement in this area of research. To reiterate this point, representative figures acquired from a bright region (white collared shirt) and a dark region (dark vest) from daguerreotype PSC 70:111 are shown in Figure 5-8. Here, the energy window has been restricted to the range 7.5 – 11 keV to allow for the deconvolution of peaks associated with Au L\(\alpha\) and Hg L\(\alpha\) within these contrasting areas. Comparing the XRF spectra from the dark vest (spectrum A) and the white collared shirt (spectrum B), a clear difference between the Au L\(\alpha\) and Hg L\(\alpha\) is observed. The bright area (spectrum B) shows a significant increase in Hg signal, due to the increase in density of image particles in highlight regions. No substantial variation between the Au fluorescence in the two spectra is expected due to the absence of a Au image (Figure 5-5D).
Figure 5-8 Spectral decomposition from the XRF spectrum collected at a bright region (white collared shirt) and a dark region (dark vest) of plate PSC 70:111.

A one-dimensional scan of the Hg L fluorescence across the chest of the seated man (Figure 5-5A) is shown in Figure 5-9. The scan, which tracks the Hg signal from the man’s right lapel (position 0 µm), vest (position 5000 µm), white shirt (position 7500 µm), vest (position 11 300 µm), and left lapel (position 12 000 µm) shows how Hg varies across the different grey tones. The greatest signal is observed across the white shirt with peaks in intensity at the edges of the jacket where highlights are observed in the image. This confirms the correlation between Hg and the image particles that increase in density where white areas are detected. Examination of the counts in adjacent positions within this line scan shows a significant variation in the Hg counts at contrast boundaries. For example, the Hg counts at the highlight of the man’s right lapel are 91 514.4 while the adjacent dark pixel of the vest has counts of 7618.9. In contrast, within the vest at neighbouring pixels, the Hg counts were 3443.1 and 3063.5. The ratio of maximum to minimum signal along the selected line of pixels is reported as 4130.
Chapter 4 discussed the use of synchrotron-based XANES spectroscopy and µ-XRF microscopy to examine a collection of tarnished 19th century daguerreotypes to characterize the tarnish products on the image surface. Not only did this work reveal information regarding the distribution of tarnish on the plate surface, but it demonstrated that SR analysis did not induce any noticeable negative optical or chemical effects due to absorbed dose, a crucial consideration when undertaking conservation science analysis. This was primarily determined through visible inspection. The absorbed dose determined by the experimental parameters used in Chapter 4 [11] to collect a series of XANES spectra (average X-ray energy = 3350 eV; incident flux = $2 \times 10^9$ photons/sec; exposure time = 90 min/region; region = 25 µm × 25 µm pixel) was over 28 million times higher, indicating that the parameters used in the current study will not impose any negative alterations to the daguerreotypes!

Figure 5-9 One-dimensional scan on the linear scale of Hg L fluorescence across the jacket lapel, vest, and white collared shirt of daguerreotype PSC 70:111.
Similar to these previous findings [11], no beam damage resulting from SR analysis was observed in this study, either visibly or through post-synchrotron SEM analysis. The absorbed dose for each sample during the XRF scan was determined to be ~ 40 Gy with the air between the daguerreotype and the detector acting as a conductive mechanism for heat removal, if any was present. While soft matter samples (such as textiles, dentine, and bone) are at a higher risk for beam damage, hard materials, such as Ag, are less prone to radiation-induced damage due to their thermal and electrical conductivity. This does not suggest that damage to hard matter samples with modern synchrotron sources is impossible [15], but that if damage is to occur, it is typically found with prolonged (i.e., scale of hours versus the 4 msec used in this study) exposure to a beam in the same spot. Moreover, reports of beam damage to hard material compounds often focus on semiconductor substrates like silicon nitride and borosilicate glasses and not on highly conducting metal such as Ag [16]. Damage to heritage objects is much more likely in studies looking at paintings under paintings [17] where the paint is far less conductive than Ag metal. However, none of those studies suggest that those exceedingly valuable paintings were damaged in any way. Thus, these combined factors would suggest that the chance of sample damage to daguerreotypes is exceedingly small. In sum, we can conclude with a fair degree of certainty that no damage occurred on the 19th century plates from this work despite its success in recovering images masked by tarnish.

5.4 Conclusions

This chapter discussed the innovative use of synchrotron-based rapid scanning µ-XRF mapping to imaging daguerreotypes that are beyond recognition. By using the Hg L emission lines and the Maia 384-element detector, entire daguerreotype plates were imaged in a non-destructive, non-invasive, and non-contact manner. The Hg map reveals fine features within the original images, even when degradation and tarnish concealed the original image from optical view. The ability to recover lost images will enable museums to expand their understanding of daguerreotype collections, as severely degraded plates would not otherwise have been able to be studied or viewed by interested scholars. Furthermore, the established method of cleaning by means of a weak NH₄OH solution appeared to have no negative impact on the concentration and distribution of Hg.
However, as no pre- and post-dip analysis was conducted, no definitive conclusions regarding the efficacy of this treatment can be made; this is currently under examination. The subsequent chapter will discuss the impact of full plate electrocleaning to the daguerreotype surface through the application of both XRF and XANES techniques.

5.5 References


Chapter 6

It is as fatal as it is cowardly to blink facts because they are not to our taste.

John Tyndall, physicist (1820 – 1893)

6 Re-Imaging 19th Century Daguerreotypes: a Soft X-ray XRF and Hard X-ray Rapid Scanning XRF Study

6.1 Introduction

The overarching goal of this chapter was to develop a means of preserving and/or conserving 19th century daguerreotypes. Synchrotron-based XRF examination was chosen, as it would allow for both a micro and macroscopic view of these plates before and after electrochemical treatment. The soft X-ray micro-characterization beamline at the CLS was chosen for its ability to locally image with XRF S and Cl, the two primary tarnish elements. The distribution and chemistry of S and Cl were tracked with X-ray absorption spectroscopy, in order to examine how each was impacted by the two differing electrocleaning methods. Entire daguerreotypes were imaged with rapid scanning XRF at CHESS [1]. The combination of the rapid scanning detection paired with higher incident energy beam allowed for the mapping of Ag, Hg, and Au across the whole surface. Comparison of elemental ratios from highlight, midtone, and shadow regions before and after cleaning provided insight into the impact of the two conservation methods. The application of scanning µ-XRF to image localized regions and entire plates provides, for the first time, a complete picture of how the electrocleaning process impacts daguerreotypes. Moreover, by collecting µ-XRF images at two different incident energies and µ-XANES, the effect of the Barger [2] and Wei [3] method on the elemental composition of the tarnished surface and the image particles and bulk can be compared.

*A version of this chapter has been published in Heritage 2019, 2.*
6.2 Materials and Methods

6.2.1 Sample Selection and Preparation

The daguerreotypes used in this study (Figure 6-1), displaying substantial surface tarnish, were supplied by the NGC. No sample preparation was required for SR analysis. While five plates were treated in this study, only three of them will be discussed.

Figure 6-1 Images of 19\textsuperscript{th} century daguerreotypes before (1) and after (2) electrocleaning with either the Barger (B) \cite{2} or Wei (W) method \cite{3}. (A) Daguerreotype (accession number PSC 70:112), NGC collection; (B) daguerreotype (accession number RCLSC1), NGC Research Study Collection; (C) daguerreotype (identified as SC1), NGC Research Study Collection.
6.2.2 Electrocleaning

Full plate electrocleaning was conducted at the NGC using the two different electrochemical methods examined: the Barger technique [2] and the Wei process [3] (see Chapter 2 section 2.4). Daguerréotype PSC 70:112 (Figure 6-1A) was treated with the Barger method. Table 6-1 outlines the differences between these two methods. The back of the plate was covered with electro-resistant tape to limit the possible interaction of Cu during the electrocleaning process. Plates RCLSC1 (Figure 6-1B) and SC1 (Figure 6-1C) were cleaned using the Wei method. After each cleaning cycle for both methods, the plate was rinsed with deionized water followed by ethanol to facilitate rapid drying. The number of cleaning cycles depended on the quality of the daguerreotype and the cleaning method chosen. Plates were cleaned until deemed appropriate by visual inspection to see if a significant amount of the tarnish had been removed, if the optical quality of the daguerreotype had been improved, and if further treatment to the artifact would negatively impact the surface. The back of daguerreotype RCLSC1 was covered while SC1 was not.

Typical total cleaning times, for both the Barger [2] and Wei [3] treatments, ranged between 20 – 40 minutes and depended on how much tarnish was present. For cleaning, the daguerreotype was secured in the bottom of a Pyrex dish between two adjustable rails. The Pt electrode was fastened at a fixed height (1 cm) above the daguerreotype. This ensured the Pt electrode remained a constant distance from the daguerreotype throughout the entire treatment while still allowing coverage of the whole plate. A schematic and details of the cleaning has been previously published [4]. The Pt electrode was directed in a circular motion over the daguerreotype during each cleaning cycle. Localized electrocleaning efforts (seen as cleaned circles in the top row of Figure 6-1) were conducted at The University of Western Ontario prior to full plate cleaning; this research will be discussed in a future publication.
Table 6-1 Summary of electrocleaning parameters used for both the Barger [2] and Wei [3] methods.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Electrolyte</strong></td>
<td>0.08 M NH₄OH</td>
<td>0.1 M NaNO₃</td>
</tr>
<tr>
<td><strong>Working Electrode</strong></td>
<td>Daguerreotype</td>
<td></td>
</tr>
<tr>
<td><strong>Counter Electrode</strong></td>
<td>Pt wire</td>
<td></td>
</tr>
<tr>
<td><strong>Working Distance</strong></td>
<td>2 cm</td>
<td></td>
</tr>
<tr>
<td><strong>Voltage Range</strong></td>
<td>5–7 DC volts</td>
<td></td>
</tr>
<tr>
<td><strong>Current Range</strong></td>
<td>15–25 mA</td>
<td>20–40 mA</td>
</tr>
<tr>
<td><strong>Temperature</strong></td>
<td>21 °C</td>
<td></td>
</tr>
<tr>
<td><strong>Cleaning Method</strong></td>
<td>Alternating between cathodic and anodic modes</td>
<td>Only cathodic cleaning (i.e., reduction occurs on the daguerreotype surface)</td>
</tr>
<tr>
<td><strong>Time Intervals</strong></td>
<td>5 minutes per cleaning mode</td>
<td>Continuous</td>
</tr>
</tbody>
</table>

6.2.3 Synchrotron Radiation Analysis

6.2.3.1 Canadian Light Source

Daguerreotypes PSC 70:112 (Figure 6-1A), RCLSC1 (Figure 6-1B), and SC1 (Figure 6-1C) were analyzed before and after treatment at the SXRMB at the CLS. Here, localized µ-XRF maps were collected with an incident energy just above the Ag L₃-edge [5]. For analysis, the daguerreotype was secured to the sample holder using alligator clips under which strips of weighing paper were placed to prevent the scratching of the surface. An incident energy of 3950 eV was selected and µ-XRF maps were created using the PFY of the elements of interest (i.e., Ag Lα (2984 eV), S Kα (2307 eV), and Cl Kα (2622 eV) X-ray emission). The spot size at the specimen was ~10 μm × 10 μm. Each
map was normalized to $I_0$ (the intensity of the incident X-ray) and analyzed using the SMAK software program [6].

Micro-XANES analysis was conducted at selected locations within each $\mu$-XRF map. X-ray absorption spectra were collected for Ag, S, and Cl in FLY mode. The parameters for each scan are summarized in Table 6-2. A series of standards (supplied by Sigma-Aldrich) were used for comparison and are included in Table 6-3. The Ag-Au alloys were produced for a previous study [7]. All absorption spectra were processed using the Athena software package [8]. Processing included energy calibration, background subtraction, normalization, and averaging of all spectra [9]. It is important to note that due to the small spot size, the position of the motors, the placement of the daguerreotype on the sample holder, and the viewing screen at the endstation, it was not possible to analyze the exact locations pre- and post-cleaning. Therefore, the XANES spectra were not collected from the exact same spot. They are, however, in the vicinity of each other and can still be used as a representation of the alteration of local chemistry from the conservation treatment. LCF analysis was conducted where appropriate; all fits are presented in Appendix F.

Table 6-2 X-ray absorption collection parameters for Ag, S, and Cl.

<table>
<thead>
<tr>
<th>Element of Interest</th>
<th>Energy Range (eV)</th>
<th>Energetic Step Size (Pre-edge)</th>
<th>Energetic Step Size (at the Edge)</th>
<th>Energetic Step Size (Post-edge)</th>
<th>Edge Jump Analyzed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>3344 – 3450</td>
<td>2.00 eV</td>
<td>0.15 eV</td>
<td>0.75 eV</td>
<td>L$_3$-edge (2984 eV)</td>
</tr>
<tr>
<td>S</td>
<td>2448 – 2554</td>
<td>2.00 eV</td>
<td>0.20 eV</td>
<td>0.75 eV</td>
<td>K-edge (2307 eV)</td>
</tr>
<tr>
<td>Cl</td>
<td>2800 – 2950</td>
<td>2.00 eV</td>
<td>0.15 eV</td>
<td>0.75 eV</td>
<td>K-edge (2622 eV)</td>
</tr>
</tbody>
</table>
Table 6-3 List of standards used for X-ray absorption near edge analysis.

<table>
<thead>
<tr>
<th>Element of Interest</th>
<th>Standards</th>
<th>Edge Jump Analyzed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>Ag, Ag(<em>{95})Au(</em>{5}), Ag(<em>{92})Au(</em>{25}), AgI, AgCl, AgBr, Ag(_2)O, Ag(_2)S, AgNO(_3)</td>
<td>L(_3)-edge (2984 eV)</td>
</tr>
<tr>
<td>Cl</td>
<td>AgCl, NaCl, KCl, HgCl(_2), Au(SMe(_2))Cl, Au(_2)Cl(_6)</td>
<td>K-edge (2307 eV)</td>
</tr>
<tr>
<td>S</td>
<td>Ag(_2)S, Na(_2)SO(_4), Na(_2)SO(_3), CuS, Cu(_2)S, HgSO(_4), Na(_2)S(_2)O(_3) • 5H(_2)O</td>
<td>K-edge (2622 eV)</td>
</tr>
</tbody>
</table>

6.2.3.2 Cornell High Energy Light Source

The conservation staff at the NGC produced individual frames for each daguerreotype prior to travel to CHESS. These frames were used to secure the plates for transport and for mounting at the beamline, thereby reducing the handling of each object.

Two beamlines (G3 and A1) were used at CHESS, Cornell University, Ithaca, NY, U.S.A. All daguerreotypes were analyzed at the CHESS facility using hard X-rays. Analysis of pre-electrocleaning samples was conducted using µ-XRF rapid scanning with a Maia-384 element detector [10] at the G3 line with an incident energy of 13 025 eV. The details of these experimental conditions have been previously discussed (see Chapter 5) [11] and the data was processed using GeoPIXE [12]. The A1 line was used to examine the daguerreotypes post-electrocleaning. Here, an incident energy of 20000 eV was used, with a dwell time of 15 ms per 50 × 50 µm pixel over a scan area of 70 × 80 mm\(^2\) for daguerreotypes PSC 70:112 (Figure 6-1A) and SC1 (Figure 6-1C) and an area of 50 × 60 mm\(^2\) for RCLSC1 (Figure 6-1B). An energy discriminating detector (Vortex ME-4 (R)), placed at about 90 degrees to the incident beam, and a XIA XMAP digital X-ray processor were used for XRF data collection. The X-ray beam incident on the sample was attenuated with Al to optimize performance of the detector. The elements of interest were Ag, Au, Hg, and Cu. The µ-XRF data was processed with PyMCA [13]. A Au foil reference (density = 19.32 g/cm\(^3\)) was employed for energy and flux calibration before scanning the samples.
To compare the amounts of Au and Hg detected before and after electrocleaning, the total Au, Hg, and Cu counts were extracted from regions of interest using GeoPIXE (before electrocleaning) and PyMCA (after electrocleaning). In order to compare both sets of XRF data, which were collected at different incident energies, the total expected fluorescence yield per mass for Cu K, Au L, and Hg L were calculated at 13 keV and 20 keV using the xraylib library [14] after normalizing to \( I_0 \). The Cu X-ray fluorescence was chosen as a reference. While it is attenuated somewhat by the Ag overlayer, Cu is unaffected by the electrocleaning process and therefore the local ratios of Au and Hg to Cu are expected to remain constant if none of the materials are affected by the treatment. Although it is not an ideal internal standard (as the Cu signal will vary based on the changing thickness of Ag and Cu), Cu was deemed the most appropriate option for a representation of the bulk material from which the examination of any variations in the surface microstructure (represented by Au and Hg that reside in the Ag-Hg-Au amalgam) could be examined. The relative expected fluorescence ratios were then calculated at each energy and the 20 keV ratios were adjusted for comparison with the 13 keV data: AuL/CuK ratios were scaled by 0.4381 and HgL/CuK ratios by 0.4388. The amounts of Au and Hg were evaluated relative to Cu by calculating the AuL/CuK and HgL/CuK count ratios. A direct comparison of raw counts was not possible because the total counts arising from the before and after scanning conditions were very different.

Three regions of interest for each image tone (highlight, midtone, and shadow) were averaged for each electrocleaning treatment, with care to select the same regions in the before and after electrocleaning datasets. Because the before and after measurements were made with different incident energies, it was important to correct the AuL/CuK and HgL/CuK ratios in the 20 keV (after) scan, taking into account the relative decrease in expected CuK fluorescence versus AuL and HgL fluorescence at the higher energy.

6.3 Results and Discussions

6.3.1 The Barger Process

While rapid scanning \( \mu \)-XRF imaging of daguerreotypes provides an alternative for plates that cannot be, or are not, improved by conservation efforts [11], the goal of museums is
still to conserve and preserve daguerreotypes. Figure 6-1A.1 and Figure 6-1A.2 shows the results of a cleaning treatment conducted on daguerreotype PSC 70:112 where a dramatic improvement in visual appearance is observed. The impact of the Barger electrocleaning method can be seen in the variation of the concentrations for Ag, S, and Cl (CLS SXRMB data in Figure 6-2). Here, the relative amount of S and Cl has notably decreased post-treatment while the counts for Ag have increased. This comparative increase in Ag is most likely due to the removal of corrosion species from the surface.

When comparing either the pre- or post-treatment Ag maps from CLS SXRMB to those collected at CHESS (either the A1 or G3 beamlines), the difference in the amount of detail observed is due to the use of different incident energies. As the details of the daguerreotype reside within the image particles, which exist in the first few hundred nanometers of the surface [15], a detailed Ag image can be obtained with the soft X-ray used at the CLS since one absorption length of Ag at the excitation energy of 3950 eV is \( \sim 0.8 \mu m \). The hard incident X-ray used at CHESS provides a bulk analysis of Ag signal as one absorption length at this energy of 20 keV (for the post-cleaning data) is \( \sim 60 \mu m \).

At the excitation energy of 20 keV, the cross-section for Ag L\(_3\) excitation is weak and the signal is dominated by the bulk, which is why the daguerreotype image cannot be observed in the CHESS Ag maps.

Figure 6-3 shows the before and after S \( \mu \)-XRF images along with accompanying XANES data for daguerreotype PSC 70:112. The before image shows a random dispersion of S across the eye region, while after cleaning, the details of the man’s right eye are apparent. The relative concentration of S correlates with regions of increased image particle (Ag-Hg-Au) density. This accumulation of tarnish in the highlight area may be due to the relative increase in reactivity in these areas. Three locations were selected for absorption analysis (i.e., examination of the local chemical environment) within the \( \mu \)-XRF image. While an effort was made to collect these spectra at the same location, it was not possible to examine the exact same sites pre- and post-cleaning. Therefore, the XANES spectra are representative of an overall change in chemistry as a result of the cleaning.
Figure 6-2 Before (top) and after (bottom) Barger electrocleaning data for PSC 70:112, which includes an optical image, μ-XRF images for Ag, Hg, and Au (hard X-ray), and μ-XRF images for Ag, S, and Cl (soft X-ray). Arrow indicates the possible use of Au leaf post-production [18].
The S K-edge, which is the result of a 1s electron being promoted to a previously unoccupied 3p orbital, occurs at 2473 eV. The location of the edge jump (peak A), along with the double feature of the first peak, suggests an Ag-S interaction [16]. While all the absorption spectra indicate Ag$_2$S to be the dominant species, the second, distinct peak at 2483 eV (peak B), indicates sulfate is also present due to surface oxidation [17].

**Figure 6-3** Before and after Barger electrocleaning data (PSC 70:112): *(left)* optical images of man’s face; *(center)* S µ-XRF images; *(right)* S K-edge XANES data collected from µ-XRF images. Regions numbered in the optical image are labeled in the XANES plot.

The quality of the spectra varies between the pre- and post-electrocleaning data (Figure 6-3). The signal to noise ratio has worsened post-cleaning due to the reduction of S on the daguerreotype surface (i.e., less S on the surface results in fewer detected counts, which produces a lower quality spectrum). In addition, while the normalization process has
produced the same area under the curve for all spectra, their non-normalized spectra look quite different. In the non-normalized spectra, the area under the curve is significantly reduced in the post-cleaning spectra, which is due to the removal of tarnish from the daguerreotype surface. The ratio between the two peaks (B/A) can be used to distinguish between the pre- and post-cleaning: before cleaning the average ratio is 0.87 while the average ratio after cleaning is 0.99. This indicates a reduction of the intensity for the sulfide peak post-cleaning, and thereby confirms the removal of sulfide and sulfate as a result of the electrocleaning process.

The impact of the Barger electrocleaning process on the Cl contamination on daguerreotype PSC 70:112 is shown in Figure 6-4. From the µ-XRF image, the tarnished surface shows a random distribution of Cl across the eye region. Post-electrocleaning, this spotted pattern has been removed and a uniform distribution, with a faint outline of the eye, is apparent. This, along with the optical image of the plate, is evidence that the conservation method was successful at returning the image as close as possible to its original state. Both of the before-cleaning absorption spectra clearly indicate the presence of AgCl as the primary tarnish product, which is clear from the location of the K-edge at 2822 eV along with the position and shape of the oscillations after the edge jump [19]. Only one of the two examined locations provided sufficient signal to collect an adequate post-electrocleaning Cl K-edge spectrum (Figure 6-4). Here, the Cl K-edge, which was collected within the vicinity of the pre-treated XAS spectra, shows a very different signature, which is similar to that of KCl [20], the source of which is unclear at this time.

During Barger electrocleaning in NH₄OH, the alternation between anodic and cathodic polarization removes the tarnish products through the oxidation and reduction of Ag on the surface of the daguerreotype. When the daguerreotype acts as the cathode, the Ag in the tarnish undergoes reduction (equations 6-1 and 6-2) while oxidation occurs at the anode, the Pt electrode.

\[
\text{Ag₂S}(s) + 2 \text{e}^- \rightarrow 2 \text{Ag}(s) + \text{S}^{2-}(aq) \tag{6-1}
\]

\[
\text{AgCl}(s) + \text{e}^- \rightarrow \text{Ag}(s) + \text{Cl}^-(aq) \tag{6-2}
\]
Barger [21] suggested that when the polarity is reversed, tarnish is removed by a mechanical action. This would be the result of the volume expansion of the underlying Ag surface caused by the Ag to Ag$_2$O reaction (equation 6-3) while at the Pt electrode reduction occurs (equation 6-4). The subsequent reversal of polarization causes the reduction of Ag$_2$O to Ag(s).

$$2 \text{Ag}(s) + 2 \text{OH}^- \rightarrow \text{Ag}_2\text{O}(s) + \text{H}_2\text{O}(aq) + e^- \quad (6-3)$$

$$\text{H}^+(g) + e^- \rightarrow \frac{1}{2} \text{H}_2(g) \quad (6-4)$$

Finally, the benefit of NH$_4$OH, which is the electrolyte in the Barger method, is that it is also a chelating agent and can chelate and remove any residual halides while the Ag$_2$S is being removed electrochemically.

![Figure 6-4 Before and after Barger electrocleaning data (PSC 70:112): (left) optical images of man’s face; (center) Cl µ-XRF images; (right) Cl K-edge XANES data collected from µ-XRF images (solid line indicates location where Cl concentration was sufficient for data collection; dotted line with an X indicates signal was insufficient for spectra collection). Regions numbered in the µ-XRF image are labeled in the XANES plot.](image-url)
Overall, a similar amount of detail is observed in both the Hg and Au CHESS images pre- and post-electrocleaning. For example, in the Hg maps in Figure 6-2, details of the foliage of the plant in the vase and the folds of the tablecloth on which it rests, and the man’s tie and tiepin are still visible after treatment. While it appears that upon further consideration that there is some minor degradation at the boundaries in the Hg map, which may corroborate the reduction in Hg signal upon treatment, due to the inherent differences in the experimental set up, these variations between the pre- and post-treatment analyses may be more a function of the scanning conditions than the electrocleaning. The quality of the Au map will depend on the initial gilding process, how the tarnish interacts with the surface and the impact of the electrocleaning process. An apparent loss of detail is seen in the Au post-treatment µ-XRF image, suggesting that this cleaning method does impact the integral elements on the daguerreotype surface.

Table 6-4 Average and standard deviation values for Au(L)/Cu(K) ratios collected before and after electrocleaning treatment for all daguerreotypes PSC 70:112 and RCLSC1. Three different areas (highlight, midtone, and shadow) were probed. The after values have been scaled to account for the difference in total fluorescence due to the different incident energies used pre- and post-treatment

<table>
<thead>
<tr>
<th>Plate</th>
<th>Cleaning Process</th>
<th>Region</th>
<th>Before Au/Cu</th>
<th>After Au/Cu</th>
<th>% Difference before/after</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSC 70:112</td>
<td>Barger</td>
<td>Highlight</td>
<td>0.012 ± 0.0010</td>
<td>0.0071 ± 0.0034</td>
<td>−41%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Midtone</td>
<td>0.0080 ± 0.0037</td>
<td>0.0050 ± 0.0017</td>
<td>−37%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Shadow</td>
<td>0.0076 ± 0.0021</td>
<td>0.0049 ± 0.0016</td>
<td>−36%</td>
</tr>
<tr>
<td>RCLSC1</td>
<td>Wei</td>
<td>Highlight</td>
<td>0.044 ± 0.0058</td>
<td>0.012 ± 0.0029</td>
<td>−73%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Midtone</td>
<td>0.050 ± 0.0030</td>
<td>0.014 ± 0.0029</td>
<td>−73%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Shadow</td>
<td>0.031 ± 0.0029</td>
<td>0.0089 ± 0.0035</td>
<td>−72%</td>
</tr>
</tbody>
</table>
Taking into account the difference in the predicted total fluorescence for the elements of interest (Cu, Au, Hg) between 13.025 keV and 20 keV incident energies, Au(L)/Cu(K) and Hg(L)/Cu(K) ratios were collected at three different regions (highlight, midtone, and shadow) pre- and post-cleaning. From examination of the Au(L)/Cu(K) ratios, the greatest difference between the pre- and post-cleaned (Table 6-4) plates is observed in the highlighted regions. This may be due to the relatively greater reactivity of the high image particle density regions compared to the shadow regions. While a decrease in Au is noted in the midtone and shadow regions of plate PSC 70:112, the loss is not as substantial as was observed in the highlighted areas. The post-electrocleaning Hg(L)/Cu(K) ratio (Table 6-5) for PSC 70:112 shows a similar (~ 40%) loss of Hg in the highlight regions. The midtone and shadow regions are more difficult to assess. The total Hg signal in these areas of the plate was low both before and after the electrocleaning process, and therefore subject to greater uncertainty than the highlighted regions.

<table>
<thead>
<tr>
<th>Plate</th>
<th>Cleaning Process</th>
<th>Region</th>
<th>Before Hg/Cu</th>
<th>After Hg/Cu</th>
<th>% Difference before/after</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSC 70:112</td>
<td>Barger</td>
<td>Highlight</td>
<td>0.0059 ± 0.0010</td>
<td>0.0034 ± 0.0010</td>
<td>−43%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Midtone</td>
<td>0.0014 ± 0.00079</td>
<td>0.0017 ± 0.00062</td>
<td>+24%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Shadow</td>
<td>n/a</td>
<td>0.0009 ± 0.0003</td>
<td>n/a</td>
</tr>
<tr>
<td>RCLSC1</td>
<td>Wei</td>
<td>Highlight</td>
<td>0.018 ± 0.0039</td>
<td>0.0033 ± 0.0010</td>
<td>−82%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Midtone</td>
<td>0.015 ± 0.0018</td>
<td>0.0027 ± 0.00090</td>
<td>−82%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Shadow</td>
<td>0.0076 ± 0.0013</td>
<td>0.0017 ± 0.00054</td>
<td>−78%</td>
</tr>
</tbody>
</table>

Table 6-5 Average and standard deviation values for Hg(L)/Cu(K) ratios collected before and after electrocleaning for PSC 70:112 and RCLSC1. Three different areas (highlight, midtone, and shadow) were probed. The after values have been scaled to account for the difference in total fluorescence due to the different incident energies used pre- and post-treatment. Positive shifts are likely related to relatively poorer signal to noise ratio and overall lower counts for Hg. (± = standard deviation).
6.3.1.1 The Wei Process

Wei’s motivation was to establish a process that utilized only the cathodic portion of the electrocleaning treatment to avoid the removal of Ag from the surface. The results presented by Wei et al. showed that the cathodic cleaning removed blue tarnish and produced a visibly improved product [3]. The visual examples provided in the Wei publication show a greater enhancement as a result of cleaning than the daguerreotypes cleaned in this study. One explanation for this discrepancy may be the relative poorer quality (i.e., the flatness or lack of depth in an image) of the plates treated in this study, thereby resulting in a less vibrant final result. This reliance on daguerreotype quality to judge the effectiveness of a conservation treatment can make developing new treatment methods challenging. However, when paired with µ-XRF, qualitative and quantitative observations can be made, thereby assisting in determining effective and safe cleaning methods.

Cleaning daguerreotype RCLSC1 with the Wei method somewhat improved the quality of the visual image (Figure 6-5). Here, the distinct border of the localized cleaning locations has been softened and the intensity of the corrosion that is present along the perimeter has been muted (Figure 6-1B.2), like that observed by Wei [3]. While the clarity of the man’s attire has improved, there appears to be a lack of depth (i.e., the attenuation of the grey scale range) in this image, which is also observed on the tarnished plate prior to treatment. This reduction in grey scale contrast produces the appearance of a flattened image, a qualitative feature that is present in both the treated and un-treated images and may indicate poorly preserved image particles. This finding suggests that the outcome of a treatment is strongly dependent on the integrity of the original surface under the corrosion layer. Therefore, despite the effectiveness of the electrocleaning technique, if a plate is of poor quality to begin with, removing the tarnish will only reveal a poor quality photograph.
Figure 6-5 Micro-XRF images from before (top) and after (bottom) Wei cleaning for RCLSC1, which includes an optical image, µ-XRF images for Hg and Au (hard X-ray), and µ-XRF images collected in the tarnish band above the man’s head for S and Cl (soft X-ray). Arrow indicates the possible use of Au leaf post-production [18].
Given the colour and location of this tarnish, it is expected to be S dominant. The CLS pre-treatment S μ-XRF image (Figure 6-5) shows a variation in concentration across the examined region, which has been removed after the electrocleaning treatment. This removal of S by the cleaning process allows for surface abrasions, such as scratches, to be visible in the μ-XRF image. The distribution of Cl on the tarnished surface shows localized hot spots of Cl build up. While a large amount of Cl was not observed on the pre-cleaned surface, the Wei method was successful at removing what was present from the surface.

In the post-treatment Au μ-XRF map, the outline of the seated man is more distinct than in the pre-treatment and the hot spot visible at the man’s ring is still apparent (Figure 6-5). A shadow-like feature that stretches across the man’s body can be seen in the Au map and to a lesser extent in the Hg image. While the source of this feature is not clear, it may be the result of how the gilding solution was applied, or simply an abrasive feature from a cloth or hand. The examination of Au(L)/Cu(K) (Table 6-4) and Hg(L)/Cu(K) (Table 6-5) ratios at highlight, midtone, and shadow regions revealed that a substantial amount of both Au and Hg have been removed as a result of the cleaning process, which is highlighted by the percent difference values in both Table 6-4 and Table 6-5. In all regions, a percent loss of approximately 72% was observed in the Au(L)/Cu(K) ratios. For the Hg(L)/Cu(K) ratios, a percent loss of 82% was noted in the highlight and midtone regions and a 78% loss in the shadow regions. This significant removal of elements integral to the plate suggests that if a daguerreotype appears to not be in a well-preserved state, that electrocleaning may further weaken the image particles through the removal of Au and Hg.

A closer examination of the local chemistry on daguerreotype RCLSC1 was conducted with XANES spectroscopy (Figure 6-6). Sulfur absorption spectra were collected from within the vicinity of two regions pre- and post-electrocleaning. Ag₂S was again observed as the dominant corrosion product with the peak at 2483 eV suggestive of sulfates, which is expected and appears to be minimal. The peak ratios for the two spectra collected from the tarnish surface correlate to the dominance of Ag₂S signal. Post-treatment, the edge jump of spectrum “After 1” has a B/A peak ratio of 0.99. This result is similar to that of
the Barger post-treatment S K-edge spectra and is indicative of the removal of sulfide groups from the surface. Similarly, in spectrum “After 2”, the reduction process has removed a significant portion of both the sulfide and sulfate groups, producing a sulfide/sulfate ratio over 1.0.

![Image](image.png)

**Figure 6-6** Before and after Wei electrocleaning data from RCLSC1: (*left*) optical images of man’s face; (*center*) S µ-XRF images collected in the tarnish above the man’s head; (*right*) S K-edge XANES data collected from µ-XRF images. Regions numbered in the µ-XRF image are labeled in the XANES plot.

Analysis of Cl within the tarnish band (Figure 6-7) shows a different distribution compared to that of S. In the tarnished Cl µ-XRF image, the only discernable features are two regions with elevated Cl signal. Post-treatment, these aggregated areas of increased Cl signal have been removed. While two areas were probed for Cl K-edge examination, only one provided sufficient signal to produce a readable spectrum. The peak positions,
widths, and relative areas vary according to the bonding state of Cl and can be used to identify the local Cl environment [22]. Analysis of the Cl K-edge data pre-cleaning (Before 1) shows a broad absorption band with a maximum located at 2824 eV. Here, the location of the edge jump, along with the post edge oscillations, corresponds to the NaCl standard [23]. This may be the result of cover glass deterioration (as discussed in Chapter 4) or from environmental contamination. In the “After 2” spectrum collected post-electrocleaning, the shift to a lower energy of the Cl edge jump is indicative of an organochlorine compound. This is most likely environmental contamination.

**Figure 6-7** Before and after Wei electrocleaning data from RCLSC1: (left) optical images of woman’s face; (center) Cl μ-XRF images; (right) Cl K-edge XANES data collected from μ-XRF images (solid line indicates location where Cl concentration was sufficient for absorption data; dotted line with an X indicates signal was insufficient for spectra collection). Regions numbered in the optical image are labeled in the XANES plot.
If the daguerreotype functions as the anode in the Wei method instead of as the cathode (which is the recommended setting by Wei), the procedure does not yield a positive outcome. Figure 6-8 shows the μ-XRF images before and after anodic treatment on the top half of the plate and cathodic cleaning on the bottom half. In the optical image, the negative impact of the oxidation (anodic treatment) is evident, as the top portion of the plate has lost its reflectivity and has gained an increased roughness, thereby masking the image and produces a negative effect on its aesthetic quality. While a loss of quality in the optical image in the top half of SC1 is observed post-treatment, the rapid scanning μ-XRF images of Hg and Au from CHESS A1 (Figure 6-8), show the main details remain in place, which suggests that this technique can be used to digitally recover the subject matter of daguerreotypes that have received unsuccessful treatments. Additional effort, such as scanning the plate twice using an incident photon energy above and below the edge of interest (HgL) would help improve the quality of the μ-XRF image, if desired.

Micro-XRF of the woman’s eye (CLS SXRMB) shows that the primary features are retained despite the anodic cleaning (Figure 6-8). The Ag and S maps, however, do show an increase in irregularity post-treatment and the contrast range in the fluorescence signal from the post-electrocleaned daguerreotypes appears to have decreased. In the pre-treatment S XRF image, the details of the eye are obvious while the finer details appear blurred in the post-treatment map. For example, the distinct line that delineates the eyelid in the before treatment map has become fragmented post-cleaning. The S K-edge spectra (Figure 6-9) that were collected pre- and post-cleaning at similar locations on the surface vary considerably. In the two spectra taken from the tarnished plate, Ag$_2$S was the dominant tarnish species. This was confirmed by comparing the “Before 1” peak ratio (0.61) to that of the Ag$_2$S standard spectrum (0.67). Examining spectrum “Before 2”, a peak ratio value (B/A) of 0.87 is determined, which corresponds to the peak ratios calculated for the S K-edge in Figure 6-3. The quality of the signal post-treatment has noticeably deteriorated with the average peak ratio for signals A and B for the three post-treatment regions being 0.99 (B/A). This is evidence that while the cleaning process has a negative effect on the quality of the image, it has also successfully removed the majority of the sulfide on the surface.
Figure 6-8 Before (top) and after (bottom) Wei electrocleaning µ-XRF images for SC1, which includes an optical image, µ-XRF images for Ag, Hg, and Au (hard X-ray), and µ-XRF images for Ag, S, and Cl (soft X-ray). The region analyzed at the CLS SXRMB is indicated in the optical image. Arrow indicates the possible use of Au leaf post-production [18].
Figure 6-9 Before and after Wei electrocleaning data from SC1: (*left*) optical images of woman’s face; (*center*) S µ-XRF images; (*right*) S K-edge XANES data collected from µ-XRF images (solid line indicates S concentration was sufficient for absorption data; dotted line indicates signal was insufficient for spectra collection).

Regions numbered in the µ-XRF image are labeled in the XANES plot.

The impact on the distribution of Cl from anodic cleaning with the Wei process can be seen in Figure 6-10. Despite the increased surface roughness caused by the treatment, the clarity of the eye is improved in the post-cleaning Cl µ-XRF map. The Cl K-edge, which occurs at 2822 eV, indicates that AgCl is the prominent deterioration compound. While these same locations were examined again post-treatment, the signal was insufficient to collect a statistically significant spectrum. A fourth location, a Cl hotspot, was subsequently examined and, when compared to the standard spectra, was determined to be KCl.
Figure 6-10 Before and after Wei electrocleaning data from SC1: (left) optical images of woman’s face; (center) Cl micro-XRF images; (right) Cl k-edge XANES data collected at select points indicated in µ-XRF images (solid line indicates S concentration was sufficient for absorption data; dotted line indicates signal was insufficient for spectra collection). Regions numbered in the µ-XRF image are labeled in the XANES plot.

Comparison of the Au(L)/Cu(K) (Table 6-6) and Hg(L)/Cu(K) (Table 6-7) ratios at highlight, midtone, and shadow regions pre- and post-cleaning was done on both the oxidized (top) and reduced (bottom) portions of the plate. Due to concerns that differing cleaning modes were not locally contained (i.e., it is suspected that the bottom right side of the place received a longer reduction treatment than the bottom left) both the left and the right sides of the plate were examined. An example of the selected regions is shown in Figure 6-11.

The left and right sides of the top (i.e., oxidized) half of daguerreotype SC1 appear to have close agreement in the highlight regions for both the Au(L)/Cu(K) and Hg(L)/Cu(K) values. Here, the greatest amount of loss is observed, for both Au and Hg; approximately
64% loss was observed for the Au(L)/Cu(K) ratios and ~40% loss was noted in the Hg(L)/Cu(K) ratios.

Table 6-6 Average and standard deviation values for Au(L)/Cu(K) ratios collected before and after electrocleaning treatment for daguerreotype SC1. Three different areas (highlight, midtone, and shadow) were probed on both the right and left sides of the plate. The after values have been scaled to account for the difference in total fluorescence due to the different incident energies used pre- and post-treatment ($\pm$ = standard deviation).

<table>
<thead>
<tr>
<th>Plate</th>
<th>Cleaning Process</th>
<th>Region</th>
<th>Before Au/Cu</th>
<th>After Au/Cu</th>
<th>% Difference before/after</th>
</tr>
</thead>
<tbody>
<tr>
<td>SC1 (left side)</td>
<td>Wei (top half; oxidation)</td>
<td>Highlight</td>
<td>0.027 ± 0.0058</td>
<td>0.010 ± 0.0046</td>
<td>-63%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Midtone</td>
<td>0.024 ± 0.0093</td>
<td>0.0090 ± 0.00069</td>
<td>-63%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Shadow</td>
<td>0.023 ± 0.0043</td>
<td>0.0087 ± 0.0012</td>
<td>-62%</td>
</tr>
<tr>
<td>SC1 (right side)</td>
<td>Wei (top half; oxidation)</td>
<td>Highlight</td>
<td>0.028 ± 0.0028</td>
<td>0.011 ± 0.0019</td>
<td>-61%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Midtone</td>
<td>0.024 ± 0.0033</td>
<td>0.010 ± 0.0015</td>
<td>-58%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Shadow</td>
<td>0.021 ± 0.0018</td>
<td>0.0086 ± 0.0010</td>
<td>-59%</td>
</tr>
</tbody>
</table>
Table 6-7 Average and standard deviation values for Hg(L)/Cu(K) ratios collected before and after electrocleaning treatment for daguerreotype SC1. Three different areas (highlight, midtone, and shadow) were probed on both the right and left sides of the plate. The after values have been scaled to account for the difference in total fluorescence due to the different incident energies used pre- and post-treatment ($\pm = \text{standard deviation}$).

<table>
<thead>
<tr>
<th>Plate</th>
<th>Cleaning Process</th>
<th>Region</th>
<th>Before Hg/Cu</th>
<th>After Hg/Cu</th>
<th>% Difference before/after</th>
</tr>
</thead>
<tbody>
<tr>
<td>SC1</td>
<td>Wei (top half; oxidation)</td>
<td>Highlight</td>
<td>0.0052 ± 0.00094</td>
<td>0.0031 ± 0.00083</td>
<td>−40%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Midtone</td>
<td>0.0030 ± 0.00021</td>
<td>0.0024 ± 0.00036</td>
<td>−20%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Shadow</td>
<td>0.0019 ± 0.000071</td>
<td>0.0020 ± 0.00013</td>
<td>+5%</td>
</tr>
<tr>
<td></td>
<td>Wei (bottom half; reduction)</td>
<td>Highlight</td>
<td>0.0060 ± 0.0010</td>
<td>0.0035 ± 0.00074</td>
<td>−42%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Midtone</td>
<td>0.0027 ± 0.00051</td>
<td>0.0022 ± 0.00035</td>
<td>−19%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Shadow</td>
<td>0.0012 ± 0.00036</td>
<td>0.0017 ± 0.00029</td>
<td>+42%</td>
</tr>
<tr>
<td>SC1</td>
<td>Wei (top half; oxidation)</td>
<td>Highlight</td>
<td>0.0050 ± 0.00059</td>
<td>0.0030 ± 0.00085</td>
<td>−40%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Midtone</td>
<td>0.0026 ± 0.00027</td>
<td>0.0023 ± 0.00012</td>
<td>−12%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Shadow</td>
<td>0.0012 ± 0.00033</td>
<td>0.0020 ± 0.00028</td>
<td>+67%</td>
</tr>
<tr>
<td></td>
<td>Wei (bottom half; reduction)</td>
<td>Highlight</td>
<td>0.0045 ± 0.00057</td>
<td>0.0032 ± 0.00076</td>
<td>−29%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Midtone</td>
<td>0.0014 ± 0.00032</td>
<td>0.0017 ± 0.00036</td>
<td>+21%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Shadow</td>
<td>0.0010 ± 0.00037</td>
<td>0.0017 ± 0.0017</td>
<td>+30%</td>
</tr>
</tbody>
</table>
Figure 6-11 Regions of interest for Au(L)/Cu(K) and Hg(L)/Cu(K) values from SC1 from both the left and right side of the plate.

The greatest difference between the top right and left sides of the plate is noted in the shadow region of the plates, with an approximate 10% difference between the two sides for Au(L)/Cu(K) and a ~60% difference observed in the Hg(L)/Cu(K) numbers. This may be the result of the inconsistent distribution of image particles observed in the shadow regions. The Au(L)/Cu(K) values for the bottom (i.e., reduction) right and left sides of the plate show a similar amount of loss across all regions (an estimated 58 – 61% loss). The right and left sides vary more significantly for the Hg(L)/Cu(K) results, with the left side showing a loss of 42%, 19% and a gain of 42% for the highlight, midtone, and shadow regions, respectively, and the right side showing a loss of 29%, a gain of 21% and 30% for the highlight, midtone, and shadow regions, respectively. Similar to the results observed for the RCLSC1 plate, which was also treated with the Wei method, the shadow (and midtone) regions are challenging to assess due to the relatively low amount of detected Hg both before and after cleaning. Moreover, while the midtone regions were taken along the bottom portions of the woman’s dress (Figure 6-11) many of the shadow regions were taken from shadows created around the woman’s hands and waist, which
reside closer to the center of the plate. In this central location, impacts of the oxidation and reduction cleaning may not be perfectly defined, thereby skewing the after cleaning ratios.

Further examination between the oxidized region (top half) and the reduction area (bottom half) shows that a similar depreciation in the Au levels was observed. As mentioned above when comparing the right and left sides of the plate, this similarity in loss of Au may be due to the challenge of localized cleaning while the entire plate is immersed in solution (i.e., while cleaning efforts were done on two different portions of the plate, some of the impact of oxidation may be observed on the bottom half of the plate and vice versa; hence, both sides of the plate was examined). One possible explanation for the similarity in values from the oxidation and reduction regions may be that the oxidized area underwent a second reduction when the bottom half of the plate was cleaned (as the reduction on the bottom half of the plate was conducted after the oxidation cleaning was done on the top half). While there are other possible reasons for the similarity observed between the two regions, we have no satisfactory explanation for the anomalous results at this time.

The variations in the Hg(L)/Cu(K) ratios in the highlight regions showed similar percent differences between the reduced and oxidized portions of the plate for the left side (~41% loss) with a 10% difference observed in the oxidation and reduction ratios from the right side of the plate. The greatest difference between the oxidized and reduced regions was observed in the shadowed regions. Given that all instances of a positive shift were observed from shadow and midtone areas where the Hg counts are low both before and after cleaning, this discrepancy is likely related to the poorer signal to noise ratio and overall lower counts for Hg in general.

It is challenging to decipher how much difference is expected due to the initial state of the plate compared to the impact of the cleaning treatment, in this case, the Wei method. However, when comparing the percent differences between plates RCLSC1 and SC1 (when reduction is used, i.e., the bottom half of the plate), plate integrity appears to make a 10% difference with respect to the Au(L)/Cu(K) ratios (i.e., 10% less Au is removed)
while it makes a 40 – 90% difference in the Hg(L)/Cu(K) ratios for highlight to shadow regions, respectively. From these preliminary conclusions, it appears that plate integrity has a greater impact on the relative amount of Hg retained after cleaning than of Au.

6.4 Conclusions

When used correctly and appropriately, full plate electrocleaning with both the Barger and Wei methods was observed to improve the optical quality of all the plates in this study. The importance of this study is in the use of synchrotron-based μ-XRF to image entire daguerreotype surfaces before and after cleaning where previously, only a localized view of any variations in chemical or physical morphology was documented. μ-XRF mapping of complete plates is essential to understand the full effect of these cleaning methods, as the impact of the treatment cannot be completely isolated (given that this treatment involves full immersion of the daguerreotype into the electrolyte). Future work should include the development of a localized, non-immersive cleaner for daguerreotypes which would ensure localized cleaning efforts, remove the need for submersion in an electrolyte, and could possibly be used to conserve coloured daguerreotypes, which are currently untreatable with electrocleaning as their colour is soluble in solution.

Along with the observation that both electrocleaning processes have the greatest impact (i.e., most significant loss of Au and Hg) on the highlight regions of the plate, it was noted that S, and sometimes Cl, accumulates within high image particle density regions, corroborating the findings in Chapter 4. X-ray absorption analysis showed that before cleaning, AgCl and Ag₂S were the dominant Ag tarnish species and that both of these compounds were removed as a result of cleaning. While Hg was removed as a result of the cleaning, the Hg XRF image was of good enough quality to retain the fine details of the photograph pre- and post-treatment. Importantly, even when electrocleaning treatment was detrimental to the surface, the Hg image preserved the original chemical signature; this may suggest that plates that have undergone unsuccessful conservation efforts may still be preserved through the digital collection of their Hg signature.

These findings can assist in influencing conservator and conservation scientists’ decisions when pursuing chemical analysis and/or conservation treatments, but each daguerreotype
must be assessed individually before proceeding. It is important to note that if a plate is of poor quality, removing the tarnish will only reveal a poor quality photograph. It may also be the case that if a daguerreotype is not well preserved, electrolycleaning will contribute to the degradation of the image. It is evident that careful consideration needs to be taken prior to undergoing electrolycleaning and that more work needs to be done before this cleaning method is deemed safe to be used on daguerreotypes.

6.5 References


Chapter 7

*The highest reward for man’s toil is not what he gets for it, but what he becomes by it.*

John Ruskin, art critic (1819 – 1900)

7 Summary and Future Work

7.1 Conclusions

This thesis showed that synchrotron radiation analysis could be applied in a non-destructive, non-invasive, and non-contact way to 19\textsuperscript{th} century daguerreotypes. The chemical speciation and distribution of the daguerreotype surface, and the tarnish that often negatively affects it, were studied with XANES, XPS, and XRF. The studies discussed within this work contribute to the synchrotron in application to arts and archaeology literature.

Chapter 1 provides an overview of conservation science, synchrotron radiation, and the application of synchrotron radiation to the cultural heritage sector. A summary of the daguerreotype production process, the deterioration that often plagues their surfaces, and a brief history of the conservation of these 19\textsuperscript{th} century images, is also discussed. An outline for the thesis is included at the end of the chapter.

Chapter 2 presents the range of experimental techniques used throughout this thesis, which includes synchrotron-based XAS, XRF microscopy, XPS, and laboratory-based XPS and SEM. The different beamlines where the synchrotron work was conducted and their experimental capabilities are also presented. The electrocleaning technique, which was the conservation technique examined in this thesis, is briefly addressed.

Chapter 3 demonstrated that synchrotron techniques, specifically XANES and XPS, could be used to examine test daguerreotypes without inducing any physical or chemical variation on the surface after exposure to X-rays. The Ag L\textsubscript{3}-edge determined that the image particles on the surface of daguerreotypes form an Ag-Au alloy with a fcc structure.
while the Au L\textsubscript{3}-edge showed that the degree of Au diffusion into the Ag plate differed between shadow and highlight areas on the surface. This was confirmed by both laboratory and synchrotron-based XPS sources. Further examination of the Au L\textsubscript{3}-edge estimated an average alloy composition of Ag\textsubscript{90}Au\textsubscript{10} for the shadow and midtone regions and an average alloy composition of Ag\textsubscript{73}Au\textsubscript{27} for the highlight region; this was attributed to the increased surface area in high particle density in the highlight regions compared to that of shadow regions, which have few to no image particles. Considering the Hg L\textsubscript{3}-edge showed the presence of metallic Hg. Although these test plates were analyzed within a few months of their production, evidence of tarnish was observed with the S K-edge, which revealed the presence of both sulfides and sulfates on the surface.

Depth profiles from XPS (laboratory source) provided further evidence for the formation of Ag-Au alloys; this was confirmed by HE-XPS Au 4f\textsubscript{7/2}/Ag 3d\textsubscript{5/2} ratios at both 3 and 8 keV incident energies. Similar to the XANES analysis of the Hg L\textsubscript{3}-edge, HE-XPS analysis did not find any substantial evidence for the presence of a Ag-Hg alloy. Both lab and SR sourced XPS showed Hg was present only within the first 1-2 nm of the surface and that alloying with Ag was possible but not consistent across all regions. It would be expected that the atomic percent values for the Ag-Hg alloys would vary across and between daguerreotypes. Importantly, if Hg is not as actively involved in amalgam formation as previously suspected, various cleaning processes, such as electrocleaning, may have a negative impact on the Hg concentration (i.e., Hg removal). This was investigated and discussed in Chapter 6.

Chapter 4 expanded beyond the proof-of-principle concept to the application of XANES and XRF to 19\textsuperscript{th} century daguerreotypes. Tarnish defects at various locations across the plate(s) and the eye region(s) were the areas of focus. Importantly, no visible alteration was noted on either of the plates post SR analysis. A variety of deterioration and types of blemishes (i.e., colourful halos, crystalline spots, and bubbles) were found to reside on the surface, suggesting an extremely complex tarnish environment. This suggests that a variety of corrosion processes take place, which is not surprising given the chemical complexity of the daguerreotype surface and its production process.
X-ray fluorescence microscopy also showed that S preferentially accumulated in high density particle regions whereas Cl appears to be more randomly distributed. Examination of the S and Cl K-edge showed the primary tarnish compounds to be Ag$_2$S and AgCl, respectively; Hg-S interactions may also be present. Similar to Chapter 3 where minimal amalgamation of Hg with Ag was observed, the presence of Hg-S bonds may suggest that Hg is more actively involved in the formation of tarnish on the daguerreotype surface than expected. However, there is insufficient evidence to support this claim at this time; an comprehensive study of the Hg L$_3$-edge should be conducted.

In Chapter 5, rapid scanning $\mu$-XRF mapping of the Hg L emission lines allowed severely degraded daguerreotypes to be imaged. Even when corrosion and degradation completely obscured the original image from view, tracking the Hg L emission revealed high-detail reproductions of the original images. This finding also corroborates the interaction of Hg with the image particles, although the extent of this amalgamation is still in question. In general, the ability to recover lost images will enable museums to expand their understanding of their daguerreotype collections, as plates that were deemed lost beyond recognition due to the severity of their degradation can now be imaged with rapid scanning XRF and subsequently studied by scholars.

The imaging of entire daguerreotypes was also addressed in Chapter 6 where rapid scanning $\mu$-XRF was used to image daguerreotypes electrocleaned with two different techniques: the Barger and Wei methods. Previously, only localized regions from electrocleaned daguerreotypes had been examined, providing only a limited scope of the impact of these treatments. The application of full plate $\mu$-XRF imaging, paired with localized XANES analysis, allowed for the full impact of these conservation efforts to be studied. In order to compare the elemental concentrations before and after treatment, Au(L)/Cu(K) and Hg(L)/Cu(K) ratios were collected from highlight, midtone, and shadow regions. In both the Barger and Wei method, Au and Hg were removed from and/or redistributed across the surface. The Barger method had the greatest impact on the relative concentrations of Au, while Hg removal appears to be similar in both cases.
As in Chapter 4, it was noted that S, and sometimes Cl, accumulates within high image particle density regions. Finally, XANES noted the presence of AgCl and Ag$_2$S before cleaning and that both of these compounds were removed as a result of treatment.

### 7.2 Future Work

Throughout this thesis, the deterioration of the cover glass was postulated as a possible source for some of the tarnish features observed on the daguerreotype surface. However, as the cover glass was not analyzed in this work, no definitive conclusion could be made. Future work should include a comprehensive study where each plate’s glass is contemporaneously analyzed with the daguerreotype. For instance, if both the plate and the cover glass were imaged with µ-XRF microscopy, a chiral pair of images would be produced, thereby conclusively showing if a tarnish product could have resulted from the glass or not. Paired with XANES and HE-XPS, these corrosion products could be identified and located within both the daguerreotype and the cover glass.

Further study on the nature of Hg needs to be investigated and a comprehensive XAS study of the Hg L$_3$-edge should be completed. From the initial work conducted at the CHESS facility on Hg maps, a significant amount of information can be collected from the XRF imaging of Hg. Localized mapping of Hg could be conducted at the VESPERS beamline at the CLS and, when paired with localized XANES analysis, could elucidate further understanding of how, and to what extent, Hg is amalgamated in the Ag-Hg image particle and if Hg is involved in the formation of tarnish (i.e., Hg-S or Hg-Cl interactions). Additionally, while the Au L$_3$-edge was examined on the daguerreotype test plates in Chapter 3, it was not analyzed on the 19th century plates. A study focusing on the Au L$_3$-edge would provide further information on the Ag-Au alloy, how it varies across the surface, and how various conservation treatments impact it.

The largest obstacle for the electrocleaning method is the necessity of full plate immersion in a suitable electrolyte. While a preliminary XANES and XRF study on the effect of different electrolytes during electrocleaning of daguerreotypes is currently being investigated by our group, additional research needs to be conducted to identify a more appropriate electrolyte. The process of electrocleaning automatically excludes the
treatment of hand coloured daguerreotypes as submersion of a coloured plate could cause the removal of the soluble pigment. Therefore, the development of a localized, non-immersive electrocleaning method would greatly benefit daguerreotype collections, either through the application of a localized electrocleaning pencil [1,2] or through the use of conducting electro gels [3,4]. Automating the cleaning process would also be a valuable pursuit. The conservator’s goal is to have as minimal an impact as possible on any object. Therefore, establishing a localized cleaning method would benefit any daguerreotype whether or not it was hand coloured.

7.3 References


Appendix A: Copyright Release from NRC Research Press

Title: The application of XANES for the examination of silver, gold, mercury, and sulfur on the daguerreotype surface

Author(s): Madalena Kozachuk, T.K. Sham, Ron Martin, et al.

Publication: Canadian Journal of Chemistry

Publisher: NRC Research Press

Date: May 15, 2017

Notes: After publication, authors retain the right to:

- Post the submitted or accepted version of the manuscript to a preprint server, institutional repository, personal website, or funder archive;
- Reproduce the manuscript for the purpose of teaching (this right extends to any academic institution where they work at the time); and
- Reuse the manuscript (in full or in part) in other works created by them for noncommercial purposes, provided the published version of record is acknowledged and cited.
Appendix B: Copyright Release from Alexandru Ioan Cuza University Publishing House

Title: X-ray photoelectron spectroscopy in the study of the chemistry of a daguerreotype surface

Author(s): Madalena Kozachuk, T.K. Sham, Ron Martin, et al.

Publication: International Journal of Conservation Science

Publisher: Alexandru Ioan Cuza University Publishing House

Date: October 2017

Notes: As an author, you retain rights for large number of author uses, including use by your employing institute or company. These rights are retained and permitted without the need to obtain specific permission from Editor. These include:

- The right to read, download, copy, distribute, print, search or link to full texts of the articles;
- The right to present the journal article at a meeting or conference;
- The right to include the journal article, in full or in part, in a thesis or dissertation;
Appendix C: Copyright Release from Nature Publishing Group

**Title:** Recovery of degraded-beyond-recognition 19th century daguerreotypes with rapid high dynamic range elemental X-ray fluorescence imaging of mercury L emission

**Author(s):** Madalena Kozachuk, T.K. Sham, Ron Martin, et al.

**Publication:** Nature Scientific Reports

**Publisher:** Nature Publishing Group

**Date:** June 22, 2018

**Notes:** This work is licensed under the Creative Commons Attribution 4.0 International License, which permits unrestricted use, distribution, modification, and reproduction in any medium, provided you:

- Give appropriate acknowledgment to the original author(s) including the publication source,
- Provide a link to the Creative Commons license, and indicate if changes were made (https://creativecommons.org/licenses/by/4.0/)

This Article contains typographical errors in the Methods Section.

Correction to: *Scientific Reports* https://doi.org/10.1038/s41598-018-27714-5, published online 22 June 2018, was released on 9 August 2018.
Appendix D: Copyright Release from Springer Publishing

**Title:** Exploring tarnished daguerreotypes with synchrotron light: XRF and µ-XANES analysis

**Author(s):** Madalena Kozachuk, T.K. Sham, Ron Martin, et al.

**Publication:** Heritage Science

**Publisher:** Springer International Publishing

**Date:** March 6, 2018

**Notes:** The open access articles published in Springer Open's journals are made available under the Creative Commons Attribution (CC-BY) license, which means they are accessible online without any restrictions and can be re-used in any way, subject only to proper attribution (which, in an academic context, usually means citation).

The re-use rights enshrined in our license agreement (http://www.springeropen.com/get-published/copyright/copyright-and-license-agreement).
Appendix E: Copyright Release from IUCr

**Title:** Eyeing the Past: Synchrotron $\mu$-XANES and XRF Imaging of Tarnish Distribution on 19th Century Daguerreotypes

**Author(s):** Madalena Kozachuk, T.K. Sham, Ron Martin, et al.

**Publication:** Journal of Synchrotron Radiation

**Publisher:** International Union of Crystallography

**Date:** September 2019

**Notes:** Authors retain the following rights to re-use the article, as long as it is not sold or reproduced, in whole or in part, for commercial purposes, *i.e.* for monetary gain on the authors' account or on that of a third party, or for indirect financial gain by a commercial entity. These rights apply *without needing to seek permission* from the IUCr.

Provided that a full bibliographic reference to the article as published in an IUCr journal is made, authors may:

- Share print or electronic copies of the article with colleagues;
- Use all or part of the article and abstract, without revision or modification, in theses and/or dissertations, in personal compilations or other publications of their own work (and may receive a royalty or other payment for such work);
- Use the article within their employer's institution or company for educational or research purposes, including use in course packs;
Appendix F: Linear Combination Fit Results for all Relevant Absorption Spectra

Appendix F 1 Linear combination fit results for the Ag L_{3}-edge in Figure 3-3. Absorption data: \(\mu\) (blue line); linear combination fit (red line); difference spectra (green line); fit range (grey lines).

Appendix F 2 Linear combination fit results for the Au L_{3}-edge in Figure 3-3. Absorption data: \(\mu\) (blue line); linear combination fit (red line); difference spectra (green line); fit range (grey lines).
Appendix F 3 Linear combination fit results for Ag L₃-edge, Cl K-edge, and S K-edge in Figure 4-8. Absorption data: µ (blue line); linear combination fit (red line); difference spectra (green line); fit range (grey lines).
Appendix F 4 Linear combination fit results for Ag L₃-edge, Cl K-edge, and S K-edge in Figure 4-9. Absorption data: \( \mu \) (blue line); linear combination fit (red line); difference spectra (green line); fit range (grey lines).

Appendix F 5 Linear combination fit results for Ag L₃-edge, Cl K-edge, and S K-edge in Figure 4-10. Absorption data: \( \mu \) (blue line); linear combination fit (red line); difference spectra (green line); fit range (grey lines).
Appendix F 6 Linear combination fit results for Cl K-edge and S K-edge in Figure 4-11. Absorption data: \( \mu \) (blue line); linear combination fit (red line); difference spectra (green line); fit range (grey lines).
Appendix F 7 Linear combination fit results for Ag L\textsubscript{3}-edge, Cl K-edge, and S K-edge in Figure 4-12. Absorption data: \( \mu \) (blue line); linear combination fit (red line); difference spectra (green line); fit range (grey lines).
Appendix F 8 Linear combination fit results for the S K-edge in Figure 6-3. Absorption data: $\mu$ (blue line); linear combination fit (red line); difference spectra (green line); fit range (grey lines).
Appendix F. Linear combination fit results for the Cl K-edge in Figure 6-4. Absorption data: μ (blue line); linear combination fit (red line); difference spectra (green line); fit range (grey lines).
Appendix F 10 Linear combination fit results for the Cl K-edge in Figure 6-6. Absorption data: \( \mu \) (blue line); linear combination fit (red line); difference spectra (green line); fit range (grey lines).
Appendix F 11 Linear combination fit results for the S K-edge in Figure 6-7. Absorption data: $\mu$ (blue line); linear combination fit (red line); difference spectra (green line); fit range (grey lines).
Appendix F 12 Linear combination fit results for the S K-edge in Figure 6-9. Absorption data: $\mu$ (blue line); linear combination fit (red line); difference spectra (green line); fit range (grey lines).

Appendix F 13 Linear combination fit results for the Cl K-edge in Figure 6-10. Absorption data: $\mu$ (blue line); linear combination fit (red line); difference spectra (green line); fit range (grey lines).
Curriculum Vitae

Name: Kozachuk, Madalena Sophia

Post-secondary Education and Degrees:
The University of Western Ontario
London, Ontario, Canada
2014-present Ph.D. Candidate

The University of Western Ontario
London, Ontario, Canada
2009-2014 B.Sc.

Honours and Awards:
Province of Ontario Graduate Scholarship
2018-2019

8th Annual Western News Newsmaker of the Year
The University of Western Ontario
2017

Technical Research Fellow
The National Gallery of Canada
Ottawa, Ontario, Canada
September-December 2017

Award for Outstanding Interdisciplinary Research
The University of Western Ontario
Faculty of Science
2015

CLS Graduate Student Travel Award
2015-2018

Related Work Experience:
Teaching Assistant
The University of Western Ontario
2014-2016

Publications:


**Conference Presentations:**


