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Synchrotron Radiation Analysis of 19th Century Daguerreotypes

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While the first commercially viable form of the photographic image, the daguerreotype, was made available in the mid-19th century, it is only recently that the chemical complexity of these extremely delicate images has started to be understood [1]. Daguerre's original production process [2] started with a highly polished, silver coated copperplate that was made light sensitive by iodine vapour. Exposure to the scene of interest photo-catalyzed the formation of silver particles on the surface whose distribution and size correlated with the intensity of the incident light. Image development was completed with heated mercury vapour and a sodium thiosulfate wash, which removed any residual silver halide, desensitizing the plate to light exposure. In subsequent years there were further advancements to this process, the most notable being the inclusion of chlorine and bromine in the sensitizing step and the use of a gold chloride thiosulfate solution to gild the surface [3].

This presentation describes a series of synchrotron experiments that was conducted on both contemporarily manufactured test plates and 19th century daguerreotypes in an effort to 1) further the understanding of the chemistry of the image, 2) characterize the distribution and speciation of tarnish on the surface, 3) optimize the X-ray fluorescence (XRF) imaging of entire daguerreotypes, and 4) develop a safe and consistent cleaning method for these historic artifacts. By working with synchrotron radiation, specifically X-ray absorption near edge structure (XANES) spectroscopy, X-ray photoelectron (XPS) spectroscopy, and XRF microscopy, a non-destructive, non-invasive, non-contact analytical method has been developed to determine the chemical and elemental composition of daguerreotypes, establishing an unparalleled and effective technique for conserving these fragile treasures.

XANES spectroscopy at the SXRMB and VESPERS beamlines at the Canadian Light Source (CLS) was used to study a freshly prepared reference daguerreotype surface [4]. The results revealed that inter-diffusion of gold (Au) and silver (Ag) has led to the development of a Ag-Au alloy and that the composition varies with depth. This was confirmed with both Ag and Au L_3-edge examination. Depth profiles from XPS provided evidence of the formation of Au-Ag alloys [5], confirmed by synchrotron-XPS Au $4f_{7/2}$/Ag $3d_{5/2}$ ratios at 3.0 and 8.0 keV, and corroborated the results from the XANES study. Examination of S and Cl in both the XANES and XPS study suggested the presence of sulfates and sulfides on the surface along with silver chloride (AgCl). These are commonly observed tarnish products on the daguerreotype surface and may be the result of incomplete washing during plate production and/or post-production contamination [6-12].

To further examine the presence of tarnish on the daguerreotype surface, XRF microscopy at the SXRMB beamline was used on 19th century daguerreotypes provided by the National Gallery of Canada (NGC) [13]. This work showed that the distributions of Ag and S were inversely correlated, suggesting a preferential accumulation of S within high-density particle regions. Silver sulfide (Ag_2S) and sulfate

(Ag_2SO_4) and AgCl were the primary tarnish features observed on the surface. Factors such as the original production and washing procedures, the storage environment and atmospheric conditions, and the possibility of previous conservation efforts will impact the integrity of the image. Clearly, these decomposition products make extremely complex tarnish substances on the surface, suggesting that the corrosion process is the result of multiple factors.

Efforts to clean these delicate surfaces have been underway in collaboration with the NGC where an improved conservation set-up has been developed and electrocleaning of entire daguerreotypes has been conducted using two different electrocleaning treatment methods [14,15]. Comparison of XRF images of these plates pre- and post-electrocleaning, which was conducted at the Cornell High Energy Synchrotron Source (CHESS), examined the effect of the conservation process on the surface. These preliminary results reveal that electrocleaning did not completely remove the integral elements (Ag, Au, and Hg) from the plate's surface. While further analysis is required before finite conclusions can be made, at this time the electrocleaning technique remains a viable prospect for safe and effective daguerreotype conservation.

Figure. 1. Before and after optical images of 19th century daguerreotype (NGC collection; accession no. PSC 70112) and accompanying Hg Lα XRF map from the un-treated plate collected at the CHESS.

This work is a significant contribution to the conservation science and museum communities within Canada and abroad. Furthermore, this project demonstrates the University of Western Ontario and the Canadian Light Source's genuine interest in fostering innovative interdisciplinary research, highlighting their dedication to the preservation and conservation of precious details of Canada's heritage. Through a partnership with the National Gallery of Canada, the dissemination and mobilization of knowledge regarding the preservation of these ethnographically significant images will ensure direct and immediate application to daguerreotype collections. This collaboration will not only provide innovative techniques and results relevant to the social science and museum communities, but also permit the general public access to these rare images [16].

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