

Part IV: Identification of the colorants in the glass support with XRF

Manganese was identified as the colorant in all five glasses. Four of the glasses also contained additional components of a soda-lime-silica glass matrix. At a scan time of 100 seconds on the portable XRF, one of the lead L_{β} lines and that arsenic K_{α} line overlap making conclusive identification of the arsenic peak difficult. In one example, Ambrotype_2, the peak for lead was very strong and distinctive, alluding to a leaded glass matrix. A representative spectrum of a non-lead containing glass from Ambrotype_1 is located in Figure 13. Table 3 is a compilation of the elements detected from each ambrotype using XRF.

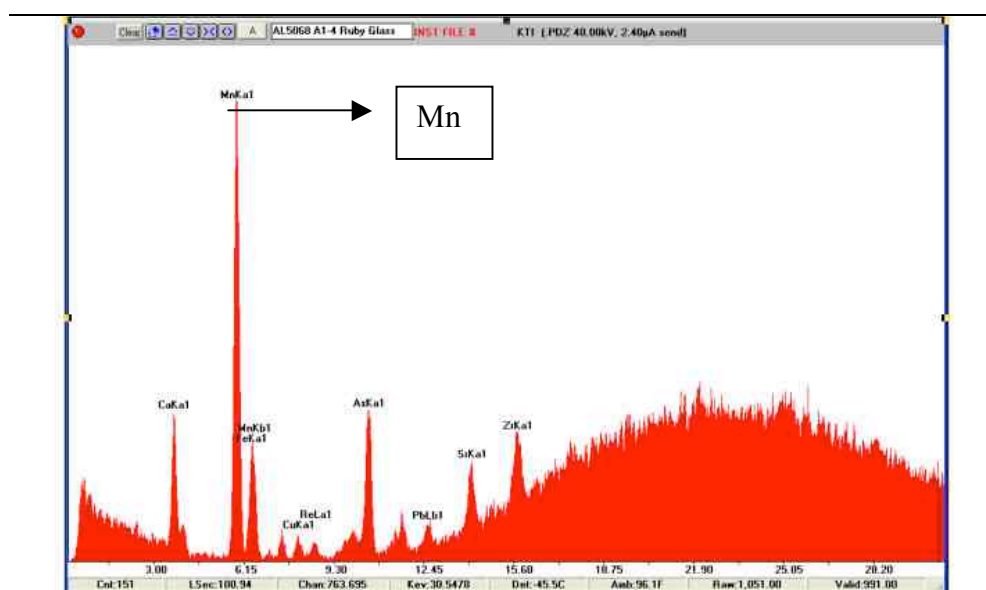


Figure 13: A representative XRF spectrum from Ambrotype_1 showing the presence of manganese.

Table 3 Data collected at 100 seconds with the portable XRF:

	Mn	Ca	As	Pb	Fe	Sr	Zr
Ambrotype_1	X	X	inconclusive	inconclusive	X	X	X
Ambrotype_2	X	X	inconclusive	X		X	X
Ambrotype_3	X	X	inconclusive	inconclusive	X	X	X
Ambrotype_4	X	X	inconclusive	inconclusive	X	X	X
Ambrotype_5	X	X	inconclusive	inconclusive	X	X	X

*Ni, Zn and Cu peaks were detected but are artifacts of the filter on the instrument

Data from the open structure XRF instrument revealed similar compositions to the portable XRF unit. Additional minor elements of Cu, K were identified and Pb was not detected. Table 4 compiles the elements detected.

For comparison, a ruby glass standard from the Winterthur collection was studied. It revealed a very different composition than the ambrotype glasses. Table 5 is a compilation of the elements found in each glass. The ruby glass standard contained gold (Au) and silver (Ag) coloring components and no manganese.

Table 4: Data collected at 100 seconds with the open structure XRF

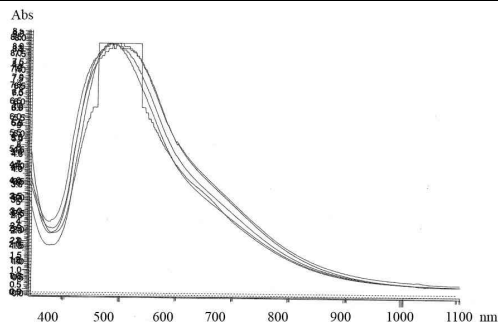
	Mn	Ca	As	Pb	Fe	K	Cu
Ambrotype_4	X	X	X		X	X	X

Table 5: A direct comparison between one ambrotype and a ruby glass, collected at 600 seconds with the portable XRF

	Mn	Si	Ca	As	Ti	Ba	Zn	Pb	Fe	Au	K	Cu	Sr	Zr	Ag	Sn
Ambrotype_3	X	X	X	X			X	X	X		X	X	X	X		
Ruby glass standard		X	X		X	X	X	X	X	X	X	X	X	X	X	X

Part V: Absorption data for ruby glass with UV/Vis spectroscopy

All five ambrotypes generated similar absorption spectra with UV/Vis spectroscopy. They all absorbed light strongly in the visible region of the electromagnetic spectrum, absorbing in the blue/ green and visible as red. There is also a slight absorbance at the shoulder of each spectrum at approximately 650nm. Table 6 shows the maximum peak absorbance for each glass support. Ambrotype_2 was optically more dense than the rest and the absorption exceeded the sensitivity of the instrument. Figure 14 is an overlay of all 5 peaks, showing their similarities. Although Ambrotype_2 was less transparent and did not generate a peak, it appears to closely follow the other curves.

Table 6		
Name	Wavelength (nm) at peak absorbance	
Ambrotype_1	488	
Ambrotype_2	Curve exceeded sensitivity of the instrument	
Ambrotype_3	495	
Ambrotype_4	498	
Ambrotype_5	506	Figure 14: Absorbance vs. wavelength (nm). Overlay of the five absorbance spectra.

Part VI: Surface analysis with SEM-EDS and BSE

Elemental mapping of the surface was carried out with SEM-EDS in four spots. Spot 4 was taken in cross-section. Figure 15 shows the locations of analysis. Table 6 is compilation of the elements found during analysis.

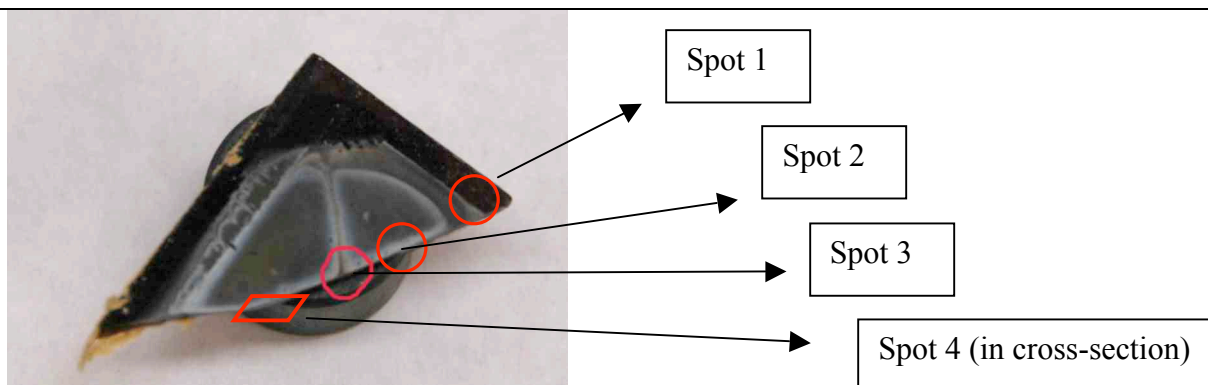
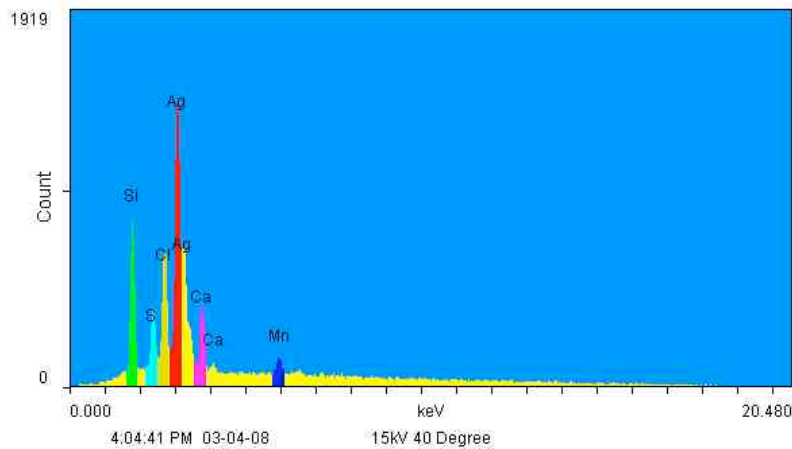


Figure 15: Areas of elemental mapping with SEM-EDS: The edge of the image layer and exposed glass support (Spot 1), the interface of tarnished and image material (Spot 2), the white tarnish (Spot 3) and in cross-section (Spot 4).

Table 6: Elements detected with SEM-EDS

	Ag	Cl	S	Ca	Mn	Si
Spot 1	X	X	X	X	X	X
Spot 2	X	X	X	X	X	X
Spot 3	X	X	X	X	X	X
Spot 4	X			X	X	X

Spot 2, revealed a distinct boundary between areas of white tarnish and areas with no white tarnish, seen in Figure 17. Spot 3, a higher magnification of an area of white tarnish, is shown below with the representative SEM-EDS map. The BSE image from the spot, displayed in Figure 18, revealed large cubic crystals above the background. Elemental mapping located chlorine (yellow), seen in Figure 19, at these crystals. In an overlay of the maps in Figure 20, the crystals also clearly contained silver (red). It is inferred from the data that silver chloride (AgCl) salts stood above a silver sulfide (Ag_2S) background. Sulfur was detected in the background and is evident by light blue pixels. The Ca, Mn and Si were all components from the underlying glass support.



Element	Color
Ag	red
Si	green
Cl	yellow
Ca	pink
Mn	dark blue
S	light blue

Figure 16: SEM-EDS elemental map and a color chart generated from Spot 3

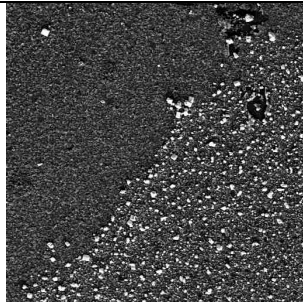


Figure 17: BSE image from Spot 2 showing the distinct line between areas of white tarnish (right) and areas not tarnished (left), 500X

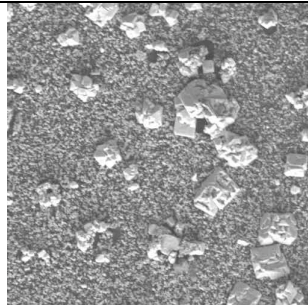


Figure 18: BSE image of surface at Spot 3 in a white tarnished area, 750X

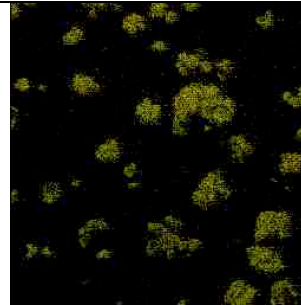


Figure 19: SEM-EDS map from Spot 3 for chlorine (yellow). It is concentrated at the crystals, 750X

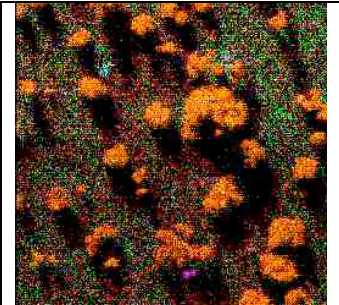


Figure 20: SEM-EDS mapping on all six elements. The crystals appear orange because of silver (red) and chlorine (yellow), 750X

Part VII: Surface analysis with Raman spectroscopy

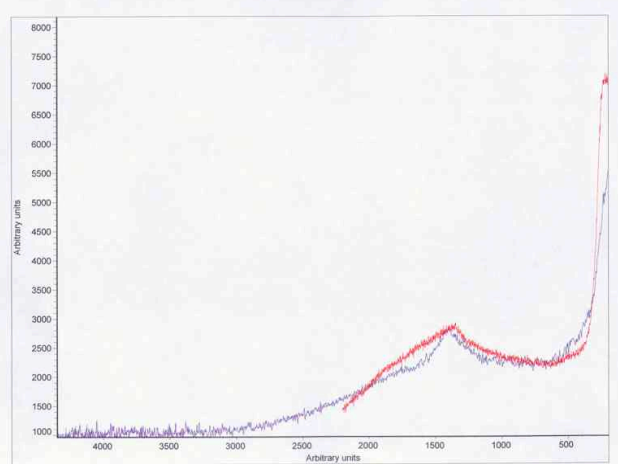


Figure 21: Raman spectra from Ambrotype_4 (red) overlaid with the reference spectra of acanthite (purple).

The spectra generated from the surface analysis of Ambrotype_1 and Ambrotype_4 matched the spectrum for acanthite, a silver sulfide mineral. An overlay of a spectrum taken in the tarnished area of Ambrotype_4 (red) and an acanthite reference (purple) is displayed in Figure 21.

4. DISCUSSION

4a. Coatings on ruby ambrotypes

Both FTIR and GC-MS revealed evidence for a varnish coating containing natural resin components. Both spectra for the GC-MS revealed a complex and somewhat confusing varnish coating. There were peaks from shellac, a common coating used historically, and also peaks coming from components of a sandarac resin, also used historically. However, there is no known mention of using shellac and sandarac in tandem. Both resins are components of spirit varnishes mixable in polar solvents but appear to have been combined with a fatty acid component, possibly a drying oil. Also, certain other unknown resin peaks were noted suggesting the presence of a complex mixture.

It is possible that the coating was an oil resin varnish which has hardened through a polymerization of oils. This was a sandarac resin and linseed oil varnish used into the 19th-century for industry. (Baade, 2008) These coatings were slow cooked under high heat and applied to a surface when cooled. The data are inconclusive since no additional fatty acids characteristic of oils were detected in these tests.

Primary texts were consulted to seek information regarding 19th-century photographic oil resin varnishes. Photographic catalogs sold proprietary ambrotype varnishes, boasting the effectiveness of these secret solutions and revealing nothing of their compositions. (Anthony's catalog, 1857) It is also known that ambrotypists made their own varnishes, following recipes outlined in journals or by word of mouth (Humphrey's Journal, 1857).

Regardless of the ingredients in the varnish, it protected the image from deterioration as the three without coatings show signs of silver tarnish. It was not discovered why ambrotypists did not coat every plate, but it was mentioned they did not like the appearance of a coated image (Burgess, 1858). It appears the aesthetic qualities of the photograph were chosen instead of protecting the image from damage.

From a conservator's perspective, once tarnish is evident it is not reversible. There is no current agreement for treating issues related to image deterioration and further discussion is beyond the scope of the study.

4b. Silver tarnish on ruby ambrotypes

Both SEM-EDS and Raman spectroscopy detected silver sulfide tarnish. The absence of chlorides detected on the surface is not surprising as the peaks were below the cutoff filter of the Raman spectrometer. They would have undoubtedly been detected given the proper instrumental conditions.

When silver is exposed to pollutants and gases in the environment it tarnishes. The mechanism is initiated in an oxidizing environment when an oxide of silver is formed at the surface. In the presence of water, these oxides provide an electrostatic potential that promotes the penetration of corrosive sulfide and chloride ions to attack the structure. (Nishimura, 2008)



Figure 22: The white haze is due to the scattering of light by silver chloride crystals. The reddish orange tarnish is silver sulfide interference colors.

Reducible sulfur is present in the atmosphere from volcanic eruptions as well as generated in combustion reactions. Chlorine components are also prevalent in the environment. They are generated industrially in combustion reactions of plastics, leaded fuels, and coal. It is a common component of particulate matter, especially in areas next to the ocean but also in areas inland.

Photographic image silver is especially vulnerable to attack. Due to the small size of silver grains, there is a large surface area for reactions to occur. Also, the silver particles above the collodion binder are exposed.

(McCormick-Goodhart, 1990, 263) In the ambrotype studies it appeared that the scattering of light by small silver chloride crystals caused the whitish haze. The colored tarnish was explained by interference from thin layers of silver sulfide. Figure 22 is a photomicrograph of the tarnish on Ambrotype_1. The presence of sulfides confirms research about tarnish published by others on the surface of cased objects. Image deterioration characterized as chloride crystals is however sparse and warrants additional research. A discussion on the significance of chloride contamination to cased objects is just beginning. Silver chloride salts are sensitive

to light and the implications of this deterioration will need to be addressed in the future.

4c. *The colorants for the ruby ambrotype glass support*

Although known as *ruby ambrotypes*, none of the 5 samples were made on a traditional ruby glass. The reddish color was not made with a precipitate of silver or gold, but colored by a complex of manganese in the glass matrix.

A recipe book from 1899 (Biser) provided a number of recipes with manganese in combination with the other metals found using XRF. The recipes for *black glass* best matched the composition. Refer to Appendix 1 for a list of recipes. In reflecting back to an 1857 photographic catalog, the word “purplish-black” glass now seems very appropriate.

Manganese is one of the oldest colorants for glass, dated to as early as 1400 BCE. Chemically, the trivalent manganese (Mn^{3+}) ion produced in a low melt and oxidizing environment, complexes with its surroundings to form a purple glass with a potential to produce a range of colors from reddish to more blue. (Weyl, 1976) The surrounding matrix and concentration are influential in determining the perceived color. The divalent manganese (Mn^{2+}) also plays a role in the color of the glass, although it is much weaker and forms complexes visible in the brown region of the spectrum. (Weyl, 1976)

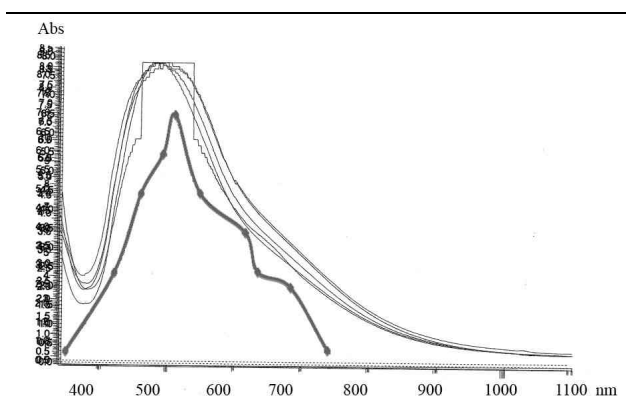


Figure 23: A resemblance between the ruby ambrotype spectra and a reference spectrum for glass with manganese in the trivalent state.

(Fedotieff, 1924) and overlaid over the five ambrotype spectra from the study, Figure 23. The resemblance is evident and even the small absorbance at the shoulder is present in all the curves.

The peak absorbance of all five ambrotype glasses matched published data for a complex of glass containing trivalent manganese (Mn^{3+}). Green and Hart (1987) studied mid 16th-century glass shards with a UV/Vis spectrometer. Presented were absorption spectra for a red glass containing Mn^{3+} in an octahedral state occurring at $\lambda_{\text{max}}=470\text{-}520\text{nm}$. Also, an absorbance spectrum of trivalent manganese glass was found

5. CONCLUSION

In this small sample of ruby ambrotypes, features not previously discussed in the literature were addressed. The primary colorant in the ruby glass was found to be manganese. The presence of an intact surface coating seems to have protected the image from silver tarnish. When the surface coating was not present, silver tarnish developed in

the image over time. The chemical composition of image tarnish found on the ruby ambrotypes was similar to that reported in previous studies of cased-photographic objects. Larger studies of ruby ambrotype images will be necessary to confirm these preliminary findings. The importance of ambrotypes as historical documents of a time period is certain and their preservation is a priority. The implications for conservation treatment and preventive measures are not formed, but are identified as areas of essential study in the future.

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Appendix 1: Black Glass Recipes

Common Glass:

Green Cullet.....100
Soda.....38
Lime.....18
Arsenic.....2

Manganese.....8
Oxide of Iron.....6
Pulverized coke.....4

Fine Glass:

Sand.....100
Potash.....36
Lime.....13
Zaffre.....10

Oxide of copper.....10
Oxide of iron.....10
Manganese10

Sand.....100
Potash.....15
Soda.....24
Lime.....18

Oxide of copper.....4
Oxide of iron.....4
Manganese.....5
Zaffre.....2

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