

XRF MEASUREMENT ERRORS IN ANCIENT AND HISTORIC SILVER ALLOY ANALYSIS: FIRST ATTEMPTS AT QUANTIFICATION

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Introduction:

Non-destructive X-ray fluorescence (XRF) quantification of silver artifacts can be hampered due to potential surface alterations during production. These surface alterations include firescale, surface porosity, and surface enrichment. The changes to surface microstructure and chemistry can drastically affect analytical results when using XRF for quantification. Sterling silver coupons were prepared using different fabrication techniques. The samples were characterized by reflected light microscopy and scanning electron microscopy (SEM). The attenuation of the XRF results was recorded. This data along with subsequent analysis will be used to create new methods of calibration to improve the reliability of this non-destructive technique of analysis.

Possible Surface Alterations

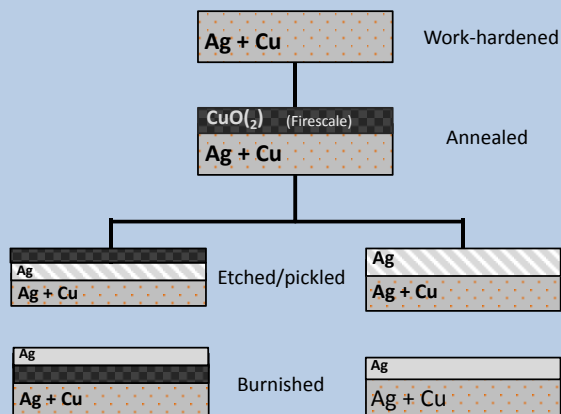


Figure 1: Surface alterations from manufacturing practices: adapted from Shugar, and Mass "Handheld XRF for Art and Archaeology", 2012: 218, 22.

Procedure:



Figure 2: From left to right Coupon 1 to 5

Steps to create surfaces observed in Figure 2:

- 1) Five coupons of sterling silver (92.5wt% Ag) were work-hardened by rolling and hammering.
- 2) Coupons 2 to 5 were annealed, allowing coupon 2 to cool and to form firescale.
- 3) Coupons 3, 4, and 5 were quenched at a black heat then etched in a solution of 1:9 distilled H₂O/H₂SO₄ to remove firescale for 5, 15, and 30 minutes respectively.
- 4) Coupons 3 to 5 were rinsed to neutralize the acid in an alkaline solution, with a final rinse in distilled H₂O
- 5) The reverse of coupons 3 to 5 were also burnished.



Figure 3: Annealing coupon



Figure 4: Coupon; cooled to black heat before quenching



Figure 5: Etching coupons

Results:

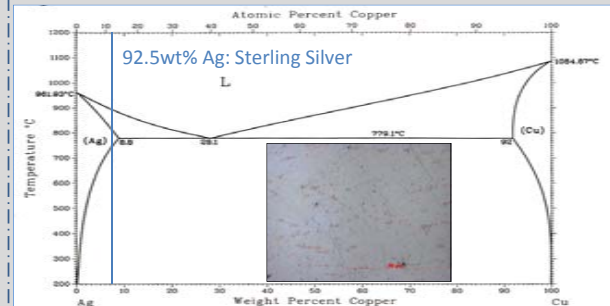
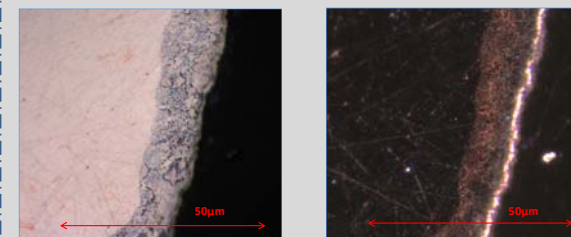


Figure 6: All coupons exhibited a consistent internal microstructure with a 92.5wt% Ag on the Ag-Cu phase diagram.



OM images of coupon 2: Figure 7 brightfield (left) and Figure 8 darkfield (right).

The black mottled layer on coupon 2 (annealed) demonstrates copper oxides forming firescale (Figure 7). In Figure 8, the copper oxide is more apparent. XRF analysis showed the firescale increased the quantified copper content and decreased the silver content, though the bulk alloy is unchanged (Table 1).

For samples that were pickled (3, 4, and 5) the removal of the copper oxide results in an increased silver quantification (Table 1). This effect is further increased when the coupons are burnished and the porosity reduced.

Any surface alterations attenuated the metal constituents in the bulk alloy (see Figure 9).

Conclusion and further research:

Surface alterations due to traditional treatments have a direct effect on XRF quantification. The extent of the effect can be measured by determining the attenuation of both silver and copper in the analytical spectra. The results are being compared to current calibration files to help determine if quantification can be improved when calibrations are combined with attenuation data.

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XRF Attenuation of Ag due to Surface Alteration

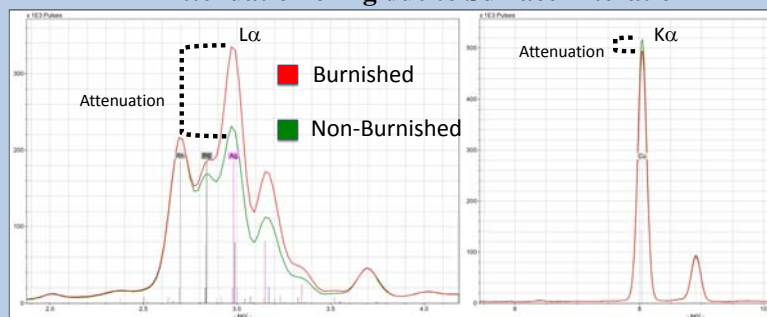


Figure 9: 15 kV 55 uA no filter, Ag (left) and (right) 40 kV 20 uA Ti/Al Filter, Cu. Bulk alloy is the same in all spectra

| Coupon # | Burnished | Ag Kα | Ag Lα | % Ag Reading from Original Lα lines |
|----------|-----------|---------|-------|-------------------------------------|
| 1 | nb | 5783630 | 91862 | ---- |
| 2 | nb | 5786124 | 88620 | 96.47 |
| 3 | nb | 5800885 | 95463 | 103.92 |
| 3 | b | 5779871 | 95714 | 104.19 |
| 4 | nb | 5796418 | 94940 | 103.35 |
| 4 | b | 5777779 | 95815 | 104.30 |
| 5 | nb | 5776051 | 94914 | 103.32 |
| 5 | b | 5775574 | 96151 | 104.67 |

Table 1: Sample of XRF area under peak; K lines are less affected than L lines (40 kV 20 uA, Ti/Al Filter).



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