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Settling for Silver: Understanding the interaction of acidified thiourea solutions and the surfaces of tarnished gilded silver objects

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Introduction

Gilded silver objects have a thin layer of metallic gold on their surfaces, but it does not prevent the underlying silver from tarnishing. An alternative to mechanical removal of tarnish via cosmetic sponge is an acidified thiourea solution. This solution forms a complex with silver sulfide, causing this tarnish layer to dissolve and be removed. Conservators noticed that after an application of acidified thiourea, objects begin to retarnish more quickly than before. One possible cause is the presence of thiourea-silver complexes remaining on the surface of the object after cleaning. Perhaps these complexes start future formations of silver sulfide tarnish. It is common practice to rinse the thiourea-cleaned area with water or ethanol afterward to remove these complexes and reduce the accelerated retarnish phenomenon. Additionally, conservators may wipe this area with a cosmetic sponge to remove residue as well.

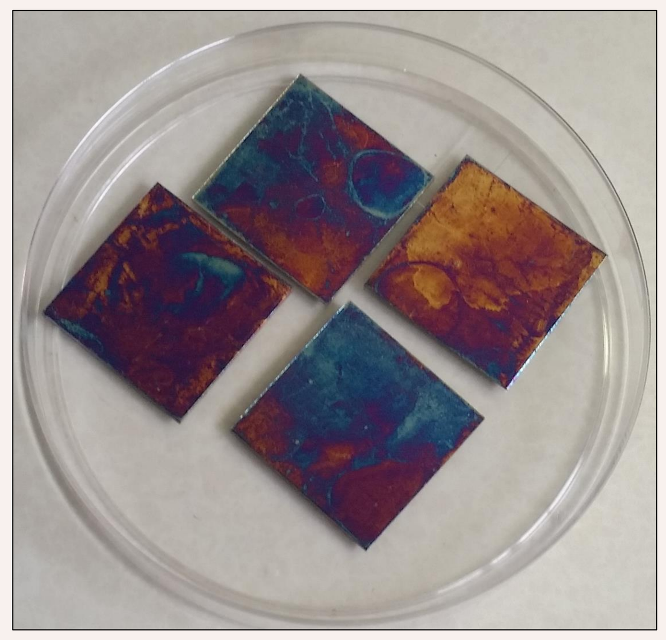
Methods

Coupon Preparation

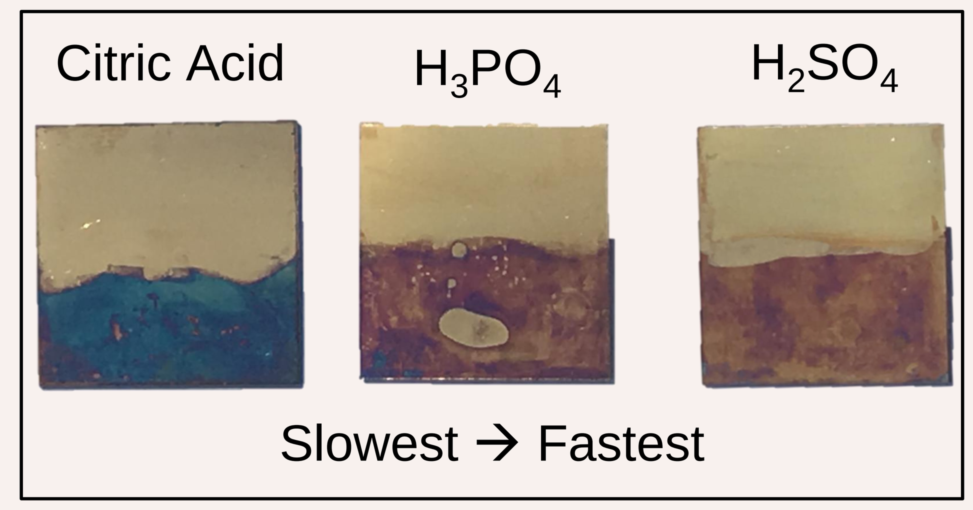
- Silver coupons were submerged in a basic solution of KCN, $KAu(CN)_2$, KOH, and KBH_4 for 15 minutes to plate a thin layer of gold (gilded).
- They were then rinsed with EtOH.
- To create an artificial tarnish, the gilded coupons were immersed in a .05% solution of K_2S for 10 minutes,
- Then they were rinsed with EtOH to remove any remaining solution.

Chemical Cleaning

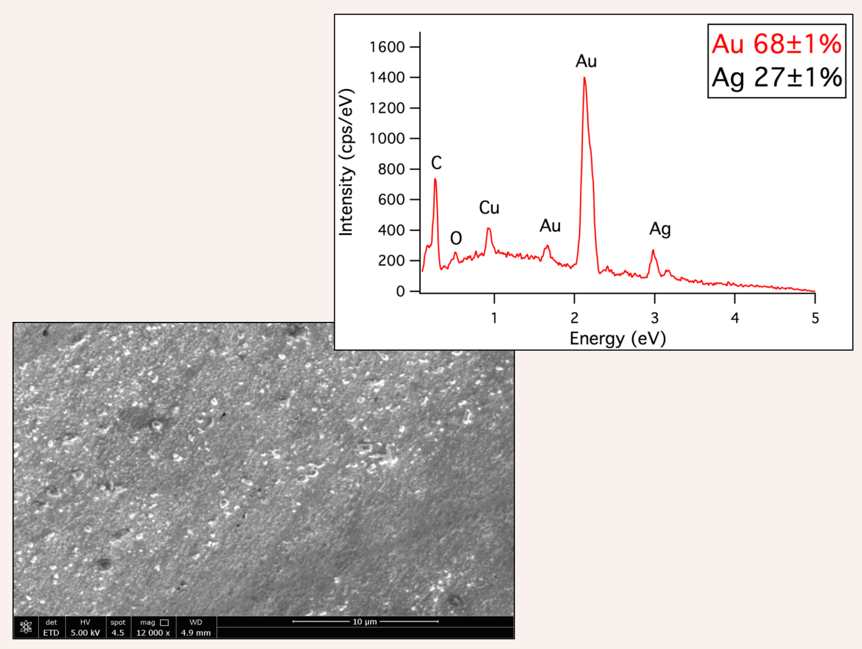
- .03 M solutions of three different types of acidified thiourea solutions were made: Phosphoric, sulfuric, and citric.
- These acidified solutions were used with a swab to clean until coupons were visibly clear of tarnish.
- Coupons were then rinsed with a swab dipped in deionized water.
- Another set of coupons for each acid were cleaned with the acidified thiourea solution, then wiped with a sponge.



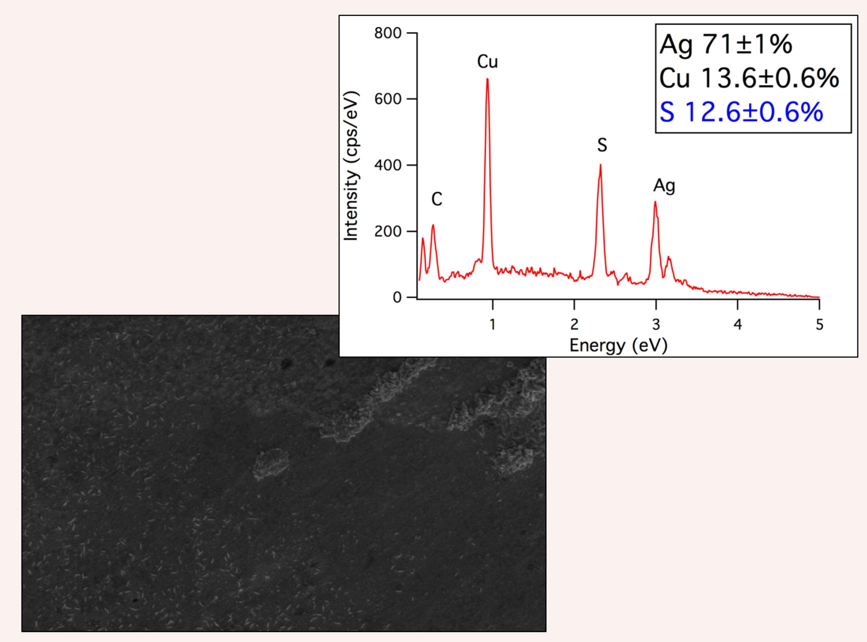
Four artificially tarnished coupons



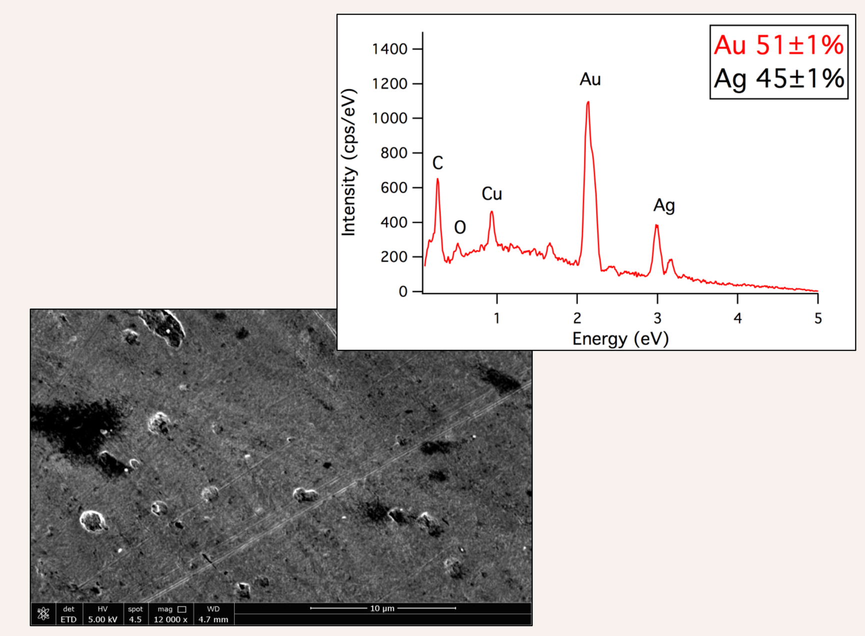
Coupon treated with: **(Right)** Sulfuric acid thiourea solution: Most effective, rapid action. (**Middle**) Phosphoric acid thiourea solution: Very effective, fast.(**Left**) Citric acid thiourea solution: Effective, not very fast acting



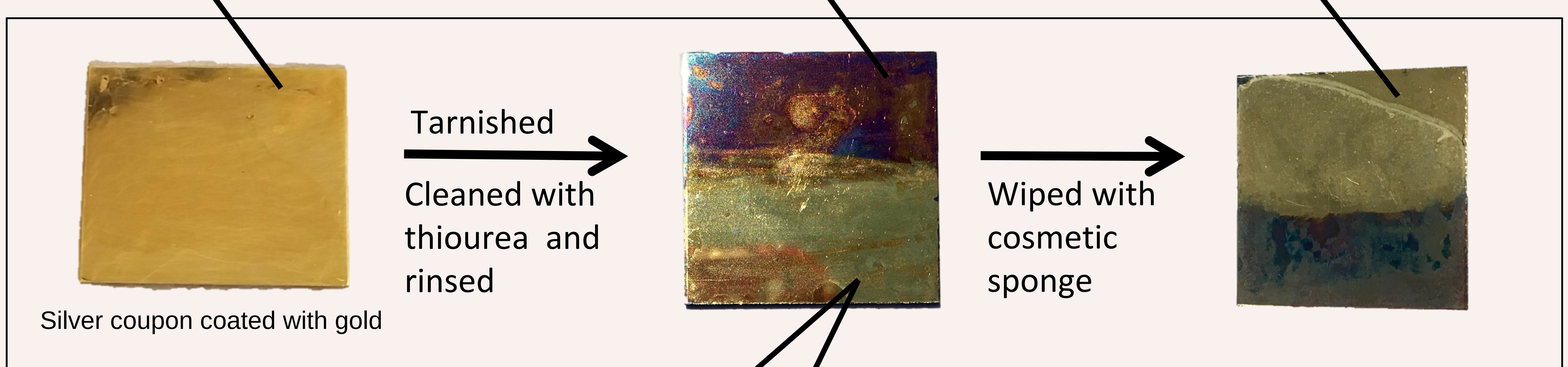
SEM micrograph of a silver coupon coated with gold and relative EDS spectrum (Inset).

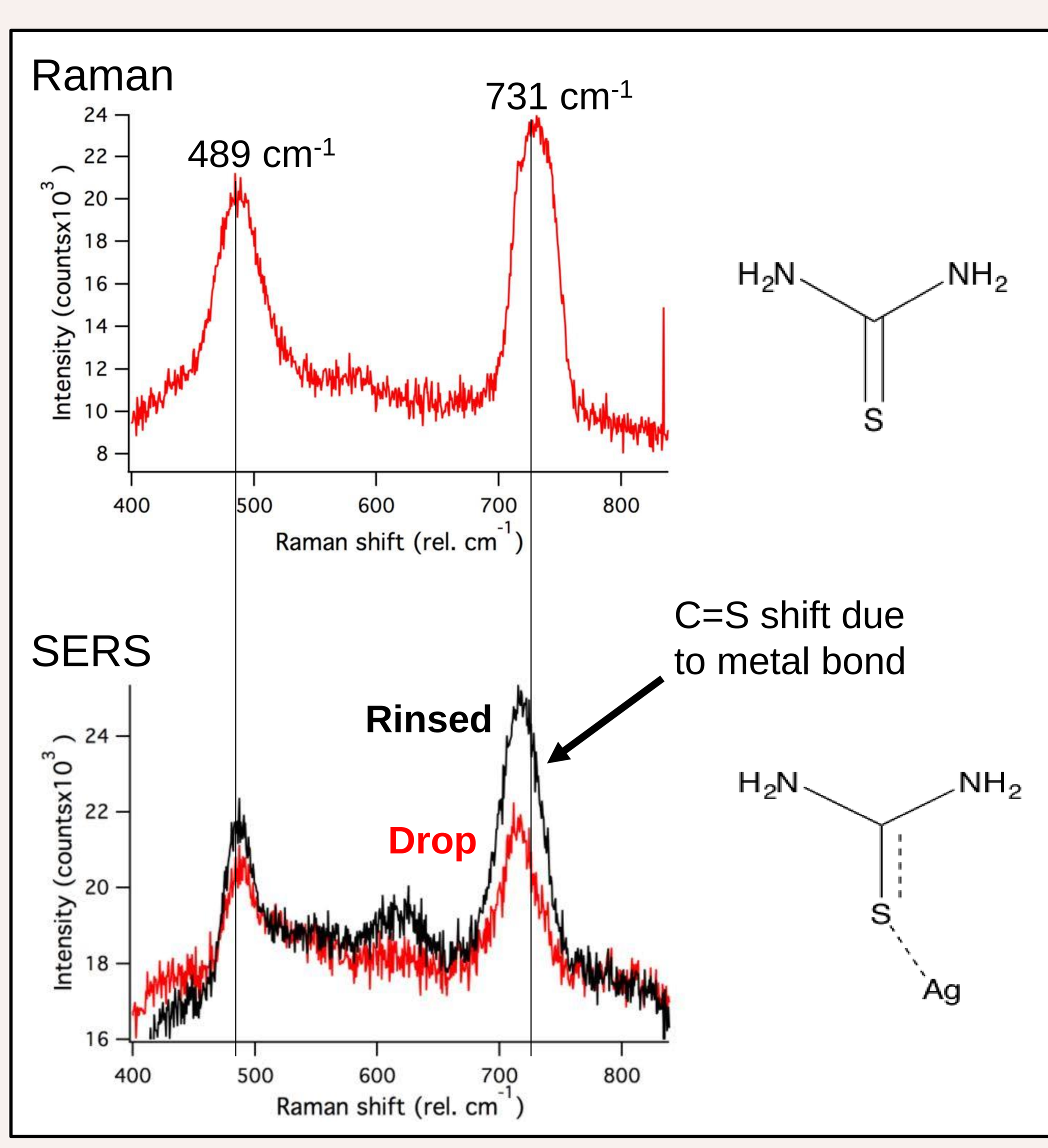


SEM micrograph of a tarnished silver coupon coated with gold and relative EDS spectrum (Inset).

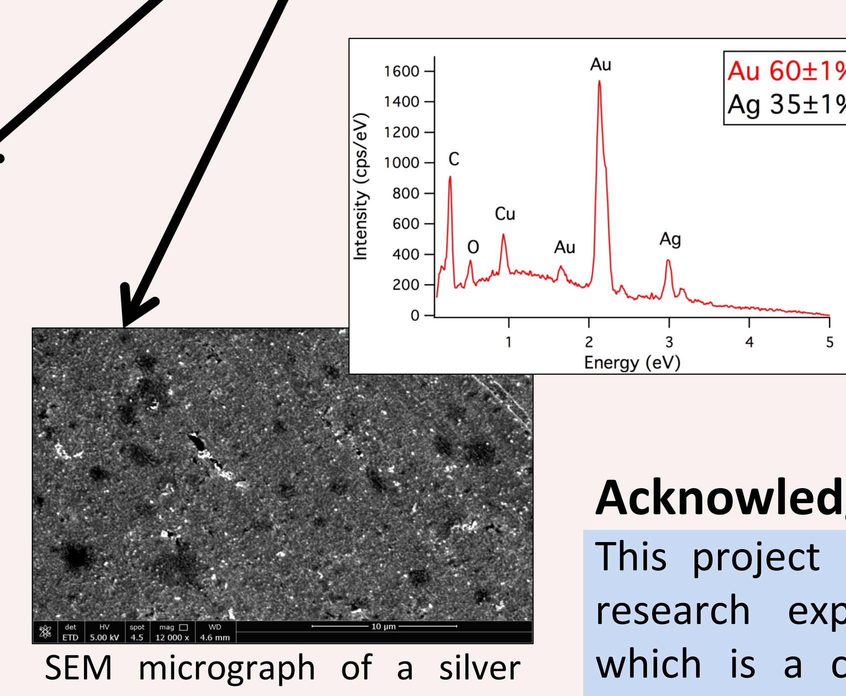


SEM micrograph of a coupon cleaned and wiped and relative EDS spectrum (Inset).





(Top): Raman spectrum of thiourea with peaks labeled. **(Bottom)**: SERS spectra of thiourea on SERS substrates before (**red**) and after rinse (**black**). Chemical structures represent the two states in which thiourea is found.



SEM micrograph of a silver coupon coated with gold and cleaned with thiourea and relative EDS spectrum (Inset).

Results

- The sulfuric acid solution was the fastest acting and most effective.
- The phosphoric acid solution was fast acting as well, but not as much as the sulfuric acid.
- The citric acid was the weakest and least effective.
- Raman spectra of the substrate after the application of acidified thiourea, showed that some thiourea complexes remained attached to the metal even after rinsing.
- It is evident that cleaning with thiourea without properly removing the solution's residue alters the object's surface.
- EDS analysis of a chemically cleaned coupon reveals a higher percentage of gold on the surface compared to a mechanically cleaned coupon, as expected.
- When the coupon is wiped, however, there is a slight decrease in the percentage of gold on the surface, indicating that some gold is removed in the wiping process.
- While wiping the cleaned surface with a sponge may remove thiourea, it also removes gold.

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