Novel Use of MA-XRF to Analyze the Efficacy of Two Common Treatments for Bronze Disease

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Introduction

The identification of bronze disease (copper chloride corrosion) is a frequent need amongst those responsible for the preservation of archaeological copper alloys as remediation is necessary to prevent severe damage from this cyclical chemical process. In addition to microchemical testing methods to identify bronze disease, a variety of analytical methods have been used for this purpose, including XRD, FTIR, Raman (Sebar et al., 2019; Porcu et al., 2022), FORS (Liu et al., 2021; Porcu et al., 2022) and µPIXE (Cruz et al., 2020). Several recent studies have also tested the application of MA-XRF for the identification of bronze disease on copper alloys with mixed success (Lins et al., 2019; Cruz et al., 2020; Di Francia et al., 2021). A recent study has utilized XRD to determine the effectiveness of treatments on copper alloys (Martín-Del-Río et al., 2018). Our study builds from this research by testing the application of MA-XRF as an instrumental method to assess the efficacy of two commonly used treatments for bronze disease, benzotriazole (BTA) and silver oxide.

Materials and Methodology

Ancient copper alloy coins exhibiting bronze disease were selected for this study by conducting a survey of the coins in the collection of the Virginia Museum of Fine Arts. Coins were initially selected based on the presence of powdery light green corrosion, a typical sign of bronze disease. The presence of bronze disease was confirmed through microchemical testing for chlorides and FTIR analysis confirming the presence atacamite/paratacamite.

The selected coins, VMFA #81.135 and VMFA #88.72 (see figures 1-2) were scanned in their entirety before treatment using the VMFA's Bruker CRONO MA-XRF with settings of 0.5mm collimator, 50kV, and 200mA to map the presence of chlorine superficially. The chloride corrosion was then mechanically removed, and the coins were treated alternately with BTA and silver oxide in an ambient lab setting followed by scanning using the same MA-XRF system and settings. The efficacy of the treatments was tested through exposure to high humidity (71% RH), based off de Alarcón (2013), by placing the coins in a sealed chamber with a potassium iodide saturated salt solution over a period of 14 days at room temperature.

Treatment Method 1 (BTA)

-The *very thin* layer of light green corrosion on 81.135 was excavated down to bare metal

-Immersion in 3% BTA in ethanol took place for approximately 1 hour and allowed to dry. The whole coin was then coated with 10% B48N in acetone.

The main complex formed from BTA is still not fully understood but pH is a known factor in formation.

Figure 1. VMFA # 81.135 Roman 1st c. CE, copper with traces of lead, arsenic, and iron, before treatment (left), after treatment (center), after exposure to high humidity (right)

Treatment Method 2 (silver oxide)

-The light green corrosion on 88.72 excavated down to the nantokite layer

-The excavated pit was spot treated with two applications of a slurry of silver oxide powder and ethanol and let dry.

Silver oxide, Ag_2O, is applied to nantokite, CuCl, to produce cuprite, Cu_2O, and silver chloride, AgCl, which are two stable products.

Figure 2. VMFA # 88.72 Roman 3-4th c. CE bronze with traces of silver, lead, and arsenic, before treatment (left), after treatment (center), after exposure to high humidity (right)

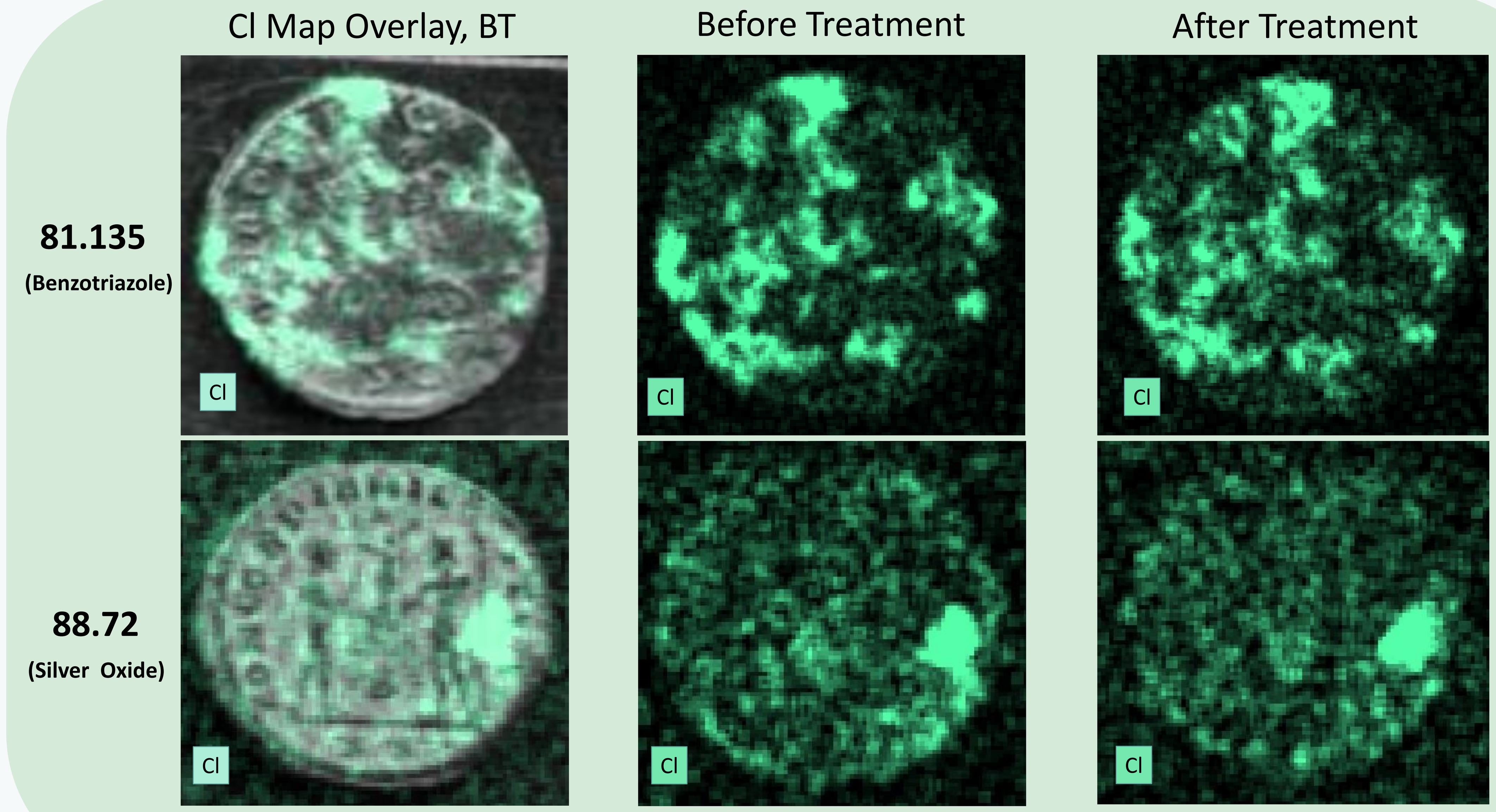

Figure 3. Results of scanning MA-XRF elemental mapping of Cl-K_α. Before treatment, Cl map overlaid on CRONO-stitched coin image (left); before treatment, Cl map (center); and after treatment, Cl map (right)

Results/Discussion

- MA-XRF was able to detect chlorine in the areas on the coins identified through microchemical testing and FTIR as bronze disease and revealed areas of chloride contamination beyond what was visible as light green corrosion on the surface (Figure 3).
- Both the BTA and silver oxide treatments were considered successful as no new bronze disease formed after exposure of the coins to high humidity for 14 days.
- Review of the MA-XRF data reveals a small reduction in chlorine on the coins:
  - For the coin treated with BTA and mechanical corrosion reduction, visual comparison of the BT and AT elemental maps show a barely perceptible decrease in Cl. This reduction in Cl correlates with a 19% decrease in the net counts for Cl (normalized to Rh) between the BT and AT XRF spectra.
  - For the coin treated with silver oxide and mechanical corrosion reduction, visual comparison of the BT and AT elemental maps show no perceptible decrease in chlorine. Comparison of the net counts for Cl (normalized to Rh) between the BT and AT XRF spectra revealed a 4% decrease in Cl after treatment.
- The continued presence of Cl in the elemental maps after treatment was expected as silver oxide combines with chloride ions to form silver chloride and BTA simply inhibits further chloride corrosion by forming a Cu-BTA complex at the object surface. However, it was surprising how little the Cl map was affected by mechanical corrosion removal.

Conclusion

Results from this study support earlier research indicating that MA-XRF has potential in the identification and mapping of chloride contamination and bronze disease on archaeological copper alloys as the elemental maps reveal areas of chlorine beyond what is visible by eye. MA-XRF, however, does not appear to be a suitable technique for determining the efficacy of bronze disease treatment methods as both methods tested (BTA and silver oxide) proved successful through high humidity exposure, yet resulted in only a very small change in the elemental maps of chlorine and other elements. Additionally, while both coins were successfully treated, the reduction in chlorine varied between the two (19% reduction and 4% reduction in net counts), suggesting that the percent reduction of chlorine counts may not be a clear indicator of treatment success.

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