Washing and Cleaning of Ancient Coins, an Alternative Method Using Ultrasound and Chemometry

G. Visco, S.H. Plattner, R. Reale and M.P. Sammartino
Rome University, La Sapienza, Pl. Aldo Moro 5, Rome, Italy

Abstract

A cleaning method is proposed, for bronze coins, involving successive washing by deionised water in ultrasonic waves bath, in order to crush and remove both soluble and insoluble corrosion products which are incoherent and not well adhering, thus all the not-protective part of the patina. The total removed incrustations was evaluated by the weight loss of the coin while, for the soluble one, chemical parameters were monitored such as anions, pH, conductivity and redox potential (ORP). All the obtained data were used for the construction of a matrix to be treated by Explorative Data Analysis (EDA) in order to enhance a trend in the washing series and to identify which variables (measures) are more correlated to the identify latent variable.

Introduction

One of the main issues a conservator of coins has to deal with is the removal of concretions and incrustations from the surface, which are not part of the coin, like, for instance, soil particles or deposits of biological origin. The next step in the cleaning procedure is the removal of soluble adhering, but not cohesive corrosion layers ("patinas"), originated by the oxidation process of the alloy. Contrarily the patina constituted by insoluble corrosion products should not be removed, or only slightly, because protective.

Obviously there is a variety of ways for removing patinas, depending also on the conservator's school and philosophical approach. Unfortunately a lot of these removal "receipts" are based more on empirical concepts than on careful chemical-physical analyses and intend to satisfy primarily aesthetic criteria than conservation ones (…because in any case a protective layer will be applied…).

The proposed scientifically based methodological approach could ensure a better conservation of bronze small objects. The use of chemometrics is not new in this field [1].

Materials & Methods

Deionised water was obtained, starting from distilled water, by a MilliQ ZFMQ 230-04 from Millipore; E50S analytical balance from Gibertini; ultrasonic bath S60H from Elma; FED53 oven from Binder; multi-parametric tester HD2156-2 from Deltaohm; 761 Compact IC from Metrohm. Software for statistic data processing are: Lotus spreadsheet 9.8 (IBM/Lotus, USA), Past 2.01 (free version by Øyvind Hammer, Norway), Datalab 2.7 (light version by H. Lohninger, Austria), WinIdams 1.3 (free version by UNESCO, France), MVSP 3.13r (shareware version by Kovach Computing Services, UK), Multivariate Analysis (an Excel ad-in by Prof. R. Brereton),

5 ancient bronze coins of the Roman Empire age, recently excavated, were used without any preliminary treatment. The coins were chosen among a total population of 153 coins of the same period by simple random sampling without replacement. After drying at 60°C with recirculating air for 30 min and successive 30 min cooling in a desiccator; the coin weight is registered; then it is placed in a 50mL centrifuge tube and 45mL MilliQ water are added. The suitably labelled tube is placed vertically by means of an appropriate holder in the ultrasonic bath filled with distilled water and set on 45 KHz; the tubes screw stopper is tightened only slightly in order to allow the outlet of eventually produced gasses.

Each wash procedure lasts 20 minutes with the sweep function activated and the heating excluded, but anyway the final temperature of the bath will reach 30-35 °C.

Once the tube is drawn out from the bath the coin is extracted by a very clean stainless steel forceps in a labelled Petri dish. The labelled tube is closed hermetically and placed in the fridge at 4°C while the coin is placed in the oven at 60°C for 30 minutes, cooled down in a desiccator and weighed. The procedure was repeated for at least seven times.

Results

Just as an example, for all the considered coins, in figs 1a and 1b the trends obtained for the percentage total weight loss (TL) and for total salts loss (TLS), as a function of the washing cycles, are compared. It can be seen that for all the coins the removal of incrustations resulted always increasing and reach more than 98% just after the first washing (fig.1a); on the contrary, the salts extraction trends are no regular and in most of the cases values obtained after the three first washings resulted lower than the final ones (fig.1b). A significant difference in the TL can be noted for the samples with the exception of coins A3-00 and A25-4005 that show a similar final percentage loss; anyway it must be pointed out that the first need two washing more to reach an almost constant weight with respect to the second so demonstrating the presence of more adhering incrustation [2]. A correlation between all the measured parameters is not easy to obtain; so a chemometric elaboration is scheduled to find a pattern/trend and will be presented in next paper.

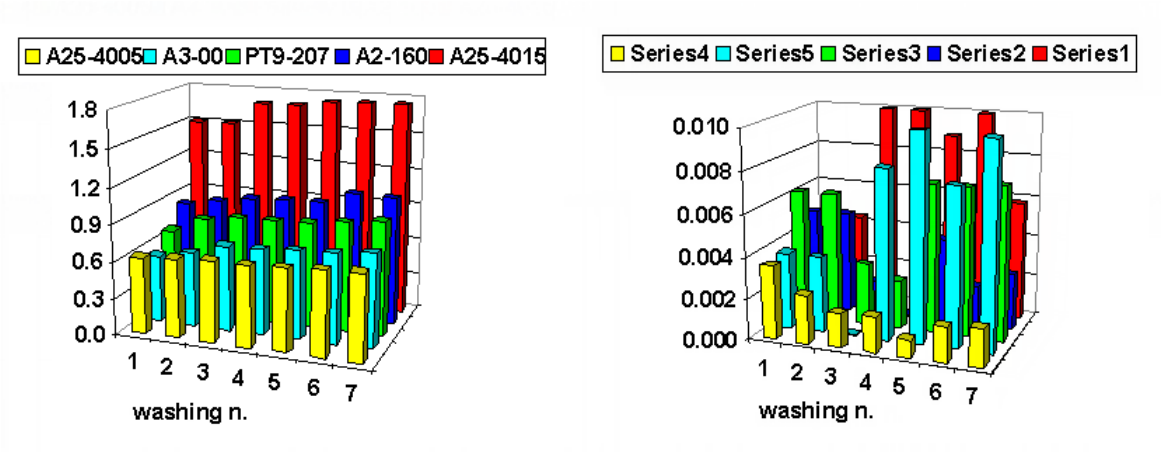

Fig 1, % total weight loss (left) and total salts loss (right) as a function of the washing cycle

Conclusions

Experimental measures demonstrated that insoluble incrustations on coins can be almost completely removed by few washing in ultrasound bath while for the soluble corrosion products, such number of washing is not sufficient. This is particularly important if we consider that chloride, i.e. the most dangerous salts for bronze, constitute the higher part of the total salts content.

References

1) K. Polikreti, V. Argyropoulos, D. Charalambous, A. Vossou, V. Perdikatsis, C. Apostolaki, Tracing correlations of corrosion products and microclimate data on outdoor bronze monuments by Principal Component Analysis, *Corrosion Sci.*, 51(10), (2009) 2416-2422

2) A. Paulina, S. Spaić, A. Zalarb, N. Trampuž-Orel, Metallographic analysis of 3000-year-old Kanalski Vrh hoard pendant, *Mater. Charact.*, 51(4), (2003) 205-218