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Feasibility of different cleaning methods for silver-copper alloys by X-ray fluorescence: Application to ancient Greek silver coins

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ABSTRACT

Archeological pieces with high Ag concentrations often have a surface enrichment of Ag. Usually, researchers in this field do not agree on the causes of these enrichments, one of which could be the cleaning procedures. In this work, a set of 18 ancient Greek silver coins was selected to study the effects of different cleaning procedures in terms of producing a surface Ag enrichment. The aim of this study is to find and select the less aggressive one in terms of the lower modification of Ag concentrations and visual aspect. These coins were analyzed by X-ray fluorescence (XRF) before and after each cleaning procedure.

1. Introduction

The analysis of elemental composition of ancient coins can provide valuable information on different aspects of life, politics, society, religion, art, culture, economy and metallurgy of minting time. Ancient coins, being precious and unique pieces, require non destructive techniques for their analysis. X-ray fluorescence (XRF) is widespread in laboratories due to its ease to use, and outside of laboratories because of the availability of portable systems. This technique is fast, sensitive, capable of simultaneous multi elemental analysis and ensures that the pieces can be quantitatively analyzed without damage.

Archeological pieces with high silver contents have often surfaces enriched by this noble metal [1–15]. Moreover, the surface enrichment of silver–copper alloy coins also depends on the different investigation depths and different acceleration voltage of incoming electrons [16]. One of the hypothesis is the cleaning procedure used to clean the coins before the measurement of its Ag content [14,15], and it is also known that the cleaning procedures can produce negative and irreversible effects on the coins [17–19]. To test this hypothesis, a set of 18 ancient Greek silver coins from the surroundings of the "Tablas de Daimiel" National Park (Villarrubia de los Ojos, Ciudad Real, Spain) and dated around the Second Punic War (218–201 B.C.) [20] was selected to be cleaned by five different cleaning procedures, namely: (1) a formic acid bath [11,21–24] diluted to 10% in demineralized water, (2) a Rochelle salts' bath (sodium potassium tartrate) [24–26] diluted to 10% in demineralized water, (3) electrochemical cleaning [27], (4) mechanical cleaning [28] and (5) laser cleaning [28,29]. All those procedures will be explained in more detail in the following section.

The 18 coins were analyzed before and after the cleaning by XRF to check the presence of ten elements (Cl, Fe, Ni, Cu, Zn, Br, Ag, Au, Hg and Bi), although only Ag, Cu, Br and Pb will be discussed in detail since the other elements do not provide useful information. The analyses were completed with Scanning Electron Microscope (SEM) images.

2. Materials and methods

2.1. Cleaning procedures

Five different cleaning procedures were used in this study to clean the coins:

1) Formic acid bath diluted to 10% in demineralized water. The coins were immersed in this bath during 6 h and after that corrosion

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products were removed from the surface by using a cotton swab. Later, the coins were introduced in demineralized water during 40 min. Finally, they were immersed in a mixture of ethyl alcohol and acetone.

2) Rochelle salts' (sodium potassium tartrate) bath diluted to 10% in demineralized water. The coins were immersed in this bath during 4 h. This procedure is the same as above.
3) Electrochemical cleaning. A little section of aluminum foil was impregnated with formic acid and it was passed punctually on the surface of the coins.
4) Mechanical cleaning. The dirt is stacked in the surface of the coins, so firstly a bamboo stick is used to take it off from the coins. Then, once the dirt is separated, it is completely removed with a brush.
5) Laser cleaning. The surface of the coins was scanned with a Nd-YAG (neodymium-doped yttrium aluminum garnet; Nd:$Y_3Al_5O_{12}$) laser and the dirt was removed.

The coins, the cleaning procedures used and the concentrations of Cu, Br, Ag and Pb before and after the cleaning are listed in Table 1, and an example of the result of each cleaning is shown in Fig. 1. Four coins were

Table 1
List of coins and concentrations and standard deviations of Cu, Br, Ag and Pb measured by XRF before and after each cleaning procedure.

			Average concentrations (% in weight)			
Coin	Face	Procedure	Cu	Br	Ag	Pb
C09-008/7	Average	Before cleaning	1.33 ± 0.38	0.62 ± 0.29	96.72 ± 0.34	0.62 ± 0.16
		Formic acid	2.03 ± 0.55	1.7 ± 1.3	95.24 ± 0.76	0.486 ± 0.085
C09-024/25	Average	Before cleaning	1.380 ± 0.088	0.126 ± 0.080	97.888 ± 0.031	0.131 ± 0.017
		Formic acid	1.75 ± 0.32	0.22 ± 0.17	97.52 ± 0.29	0.080 ± 0.016
C09-024/28	Average	Before cleaning	1.02 ± 0.14	0.46 ± 0.27	97.30 ± 0.13	0.492 ± 0.040
		Formic acid	1.100 ± 0.083	0.59 ± 0.40	97.41 ± 0.34	0.283 ± 0.020
C09-024/37	Average	Before cleaning	0.78 ± 0.22	7.1 ± 1.7	91.0 ± 1.5	0.2381 ± 0.0077
		Formic acid	0.67 ± 0.21	17.2 ± 4.5	81.5 ± 4.3	0.095 ± 0.012
C09-024/20	Obverse	Before cleaning	1.602 ± 0.086	1.367 ± 0.043	96.26 ± 0.34	0.389 ± 0.066
		Formic acid	1.60 ± 0.12	3.662 ± 0.093	94.26 ± 0.23	0.208 ± 0.021
	Reverse	Before cleaning	1.667 ± 0.050	0.986 ± 0.019	96.54 ± 0.42	0.392 ± 0.066
		Rochelle salts	1.43 ± 0.32	1.87 ± 0.68	96.29 ± 0.32	0.163 ± 0.035
C09-024/27	Obverse	Before cleaning	2.316 ± 0.010	0.109 ± 0.046	96.588 ± 0.094	0.497 ± 0.022
		Formic acid	2.8789 ± 0.0054	0.178 ± 0.051	96.173 ± 0.013	0.303 ± 0.035
	Reverse	Before cleaning	2.09 ± 0.16	0.0794 ± 0.0022	96.90 ± 0.28	0.450 ± 0.035
		Rochelle salts	2.793 ± 0.098	0.090 ± 0.033	96.45 ± 0.26	0.253 ± 0.097
C09-024/54	Obverse	Before cleaning	0.425 ± 0.011	9.02 ± 0.11	90.13 ± 034	0.069 ± 0.013
		Formic acid	0.250 ± 0.095	21.5 ± 4.8	78.0 ± 4.6	0.0220 ± 0.0032
	Reverse	Before cleaning	0.5008 ± 0.0093	14.322 ± 0.091	84.66 ± 0.24	0.085 ± 0.015
		Rochelle salts	0.236 ± 0.060	20.3 ± 6.3	79.3 ± 6.2	0.0151 ± 0.0013
C09-008/11	Average	Before cleaning	0.30 ± 0.11	1.9 ± 2.5	97.1 ± 2.3	0.1960 ± 0.0095
		Rochelle salts	0.463 ± 0.031	0.35 ± 0.23	98.58 ± 0.25	0.154 ± 0.018
C09-024/23	Average	Before cleaning	0.67 ± 0.27	2.3 ± 1.5	96.4 ± 1.2	0.0870 ± 0.0065
		Rochelle salts	0.80 ± 0.34	3.3 ± 1.0	95.39 ± 0.71	0.042 ± 0.014
C09-024/41	Average	Before cleaning	1.18 ± 0.14	0.90 ± 0.17	96.84 ± 0.26	0.198 ± 0.036
		Rochelle salts	1.65 ± 0.23	3.87 ± 0.94	93.68 ± 0.83	0.119 ± 0.020
C09-024/51	Average	Before cleaning	0.94 ± 0.13	0.39 ± 0.36	97.88 ± 0.57	0.384 ± 0.065
		Rochelle salts	1.02 ± 0.24	0.67 ± 0.75	97.79 ± 0.92	0.226 ± 0.055
C09-008/5	Obverse	Before cleaning	1.662 ± 0.085	0.1958 ± 0.0096	97.34 ± 0.32	0.323 ± 0.055
		Laser	1.956 ± 0.028	0.340 ± 0.091	97.14 ± 0.18	0.205 ± 0.016
	Reverse	Before cleaning	1.457 ± 0.038	0.363 ± 0.011	96.92 ± 0.35	0.423 ± 0.071
		Mechanical	2.01 ± 0.40	1.22 ± 0.32	95.92 ± 0.76	0.274 ± 0.046
		Mechanical + laser	1.69 ± 0.86	0.59 ± 0.26	97.18 ± 0.69	0.190 ± 0.098
C09-008/8	Obverse	Before cleaning	0.77 ± 0.26	2.76 ± 0.76	95.63 ± 0.47	0.275 ± 0.012
		Laser	2.532 ± 0.011	2.206 ± 0.088	94.64 ± 0.13	0.200 ± 0.011
	Reverse	Before cleaning	1.02 ± 0.12	1.82 ± 0.29	96.27 ± 0.11	0.332 ± 0.012
		Mechanical	1.12 ± 0.14	6.2 ± 1.5	92.1 ± 1.3	0.164 ± 0.025
C09-008/9	Obverse	Before cleaning	0.979 ± 0.052	0.362 ± 0.016	97.71 ± 0.32	0.138 ± 0.024
		Laser	1.085 ± 0.095	0.47 ± 0.11	97.765 ± 0.032	0.0661 ± 0.0040
	Reverse	Before cleaning	0.373 ± 0.012	1.708 ± 0.028	96.58 ± 0.30	0.277 ± 0.047
		Mechanical	0.709 ± 0.070	5.2 ± 3.0	93.1 ± 3.0	0.1537 ± 0.0051
		Mechanical + laser	0.812 ± 0.029	3.4 ± 1.9	95.0 ± 1.9	0.0843 ± 0.0083
C09-024/26	Obverse	Before cleaning	1.039 ± 0.070	1.77 ± 0.71	95.99 ± 0.66	0.4166 ± 0.0064
		Laser	1.98 ± 0.28	2.13 ± 0.99	95.14 ± 0.69	0.302 ± 0.025
	Reverse	Before cleaning	2.008 ± 0.097	0.144 ± 0.039	96.70 ± 0.10	0.5436 ± 0.0063
		Mechanical	2.22 ± 0.37	1.4 ± 2.0	95.5 ± 1.5	0.327 ± 0.055
		Mechanical + laser	2.236 ± 0.083	0.25 ± 0.11	96.704 ± 0.020	0.3319 ± 0.0031
C09-024/32	Obverse	Before cleaning	1.529 ± 0.076	0.1371 ± 0.0072	97.17 ± 0.39	0.106 ± 0.019
		Laser	1.899 ± 0.096	0.115 ± 0.023	97.33 ± 0.16	0.063 ± 0.012
	Reverse	Before cleaning	2.25 ± 0.13	0.2411 ± 0.0097	96.61 ± 0.32	0.167 ± 0.029
		Mechanical	2.214 ± 0.047	0.759 ± 0.063	96.24 ± 0.15	0.08665 ± 0.00071
		Mechanical + laser	2.065 ± 0.010	0.43 ± 0.27	96.85 ± 0.31	0.084 ± 0.0023
C09-024/47	Average	Before cleaning	1.66 ± 0.24	0.121 ± 0.015	96.30 ± 0.18	0.389 ± 0.066
		Electrochemical	1.97 ± 0.53	0.054 ± 0.064	96.37 ± 0.61	0.225 ± 0.053
C09-024/30	Average	Before cleaning	2.00 ± 0.15	0.021 ± 0.030	96.41 ± 0.86	0.322 ± 0.012
		Electrochemical	2.06 ± 0.13	0.046 ± 0.053	97.092 ± 0.078	0.148 ± 0.025