A comparative analysis of old and recent Ag coins by XRF methodology

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Abstract

The investigation of silver coins dated since the first century B.C. up to recent times, coming from different countries in the world, has successfully generated a growing interest among numismatic researchers. The classification of these coins into originals, copies and imitations - according to their provenance and to their Ag content - has been performed by using the X-ray fluorescence (XRF) analysis. The archaeological challenge is to explain the large diversification of these coins, to determine the differences in composition, weight and physical aspects. A non-destructive physical method was employed to study the properties of silver coins (as in this case) allowing a detailed characterization of the analyzed samples. The XRF analysis was applied to the bulk, through an X-ray tube, and to the surface patina, through an electron beam.

Introduction

The growing interest in the archaeological research techniques is important to have detailed evidence of the history and culture of the past. In particular our attention has focused on XRF analysis of silver coins. The samples originate from the first century B.C. until today, coming from different countries whose study has recently gained value relatively to their origin context, allowing to get historical information. A fundamental problem deals with the classification of these coins into originals, copies and imitations, according to their provenance and to their silver content. In the last years, Greek and Roman Ag coins have been well classified by means of the X-ray fluorescence (XRF) analysis [1, 2]. The archaeological problem arises from the necessity to explain the large

diversification of these coins, as well as the differences in composition, weight and physical aspects [3]. Ancient and recent coins usually have a roughly homogeneous core and mostly thin surface layer with different composition and varying thickness. This layer can be silver enriched, oxidized, corroded or soiled. Therefore, the application of a non-destructive physical method represents a powerful tool to investigate the properties of silver coins. We adopted the XRF analysis with an X-ray tube to study deep layers, while for surface layers an electron beam was employed [4].

Materials and methods

We prepared an experimental set-up, in which each coin was examined by the XRF technique using an X-ray tube at 23 kV

voltage and 15 μA current using an Ag anode (Amptek), besides to a 20 keV electron microprobe of a SEM microscope (Fei Quanta Inspect) [5]. A Si(Li) detector, cooled by Peltier effect, was employed to detect photons between 1 and 20 keV energy with an energy resolution of 190 eV FWHM at 5.9 keV, with a typical acquisition time of 30 minutes.
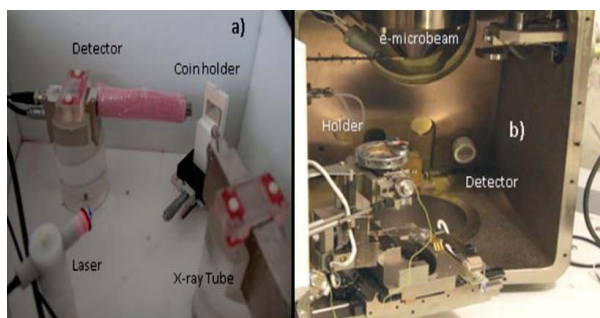

Fig. 1. Experimental set-up of the XRF systems using a) X-ray tube and b) an e-microbeam.

Fig. 1 shows a picture of the XRF systems using a) X-ray tube and b) an e-microbeam.

The XRF analysis using X-ray tube was performed in air adopting a coin-detector distance of 2.5 cm, while the analysis carried out by means of an e-microbeam was conducted in high vacuum (10^{-6} mbar).

Pure thick Ag sheets, supplied by Goodfellow, were used as certified reference materials, and irradiated under the same conditions as the samples investigated. All analyzed coins were chemically and, in some cases, mechanically cleaned to remove any eventual dirtiness trace.

The 23 keV photons supplied by the X-ray tube in Ag bulk have an absorption mass coefficient of about 10 cm^2/g; the Ag thickness at which the initial intensity I_0 decreases to 1% is about 460 μm, according to NIST database [6]. In addition, 20 keV electrons in Ag bulk have a range of about 0.5 μm, evaluated by SREM code [7], therefore the estimated composition will refer to the bulk if using the X-ray tube, while regarding

only to the surface layers if we employ the SEM electron microbeam.

We analyzed two sets of silver coins: the old Ag coins and the recent ones.

The 'ancient' group includes: #1) Greek Tetradrachms from Messana, 470–466 B.C.; #2) Greek Tetradrachms from Messana, 470–466 B.C. (counterfeit); #3) Roman Denarius, II Cen. A.C.; #4) Alexander the Great, Drachma, IV Cen. A.C.; #5) Gigliato Roberto D'Angiò, XIV sec. A.C. (counterfeit). The 'recent' group includes: #6) 1 Swiss Franc, 1934; #7) Quarter Dollar, USA, 1943; #8) 5 Lire, Vittorio Emanuele, Italy, 1945; #9) 500 Lire, Caravelle, Italy, 1960; #10) 500 Lire, Guglielmo Marconi, Italy, 1974. The photos of the ten coins are reported in Fig. 2.

Fig. 2. Picture of the ten analyzed coins.

The Ag content in the bulk composition of each coin was measured with respect to the standard calibration sample. Different thickness samples were used, namely from 0.5 mm up to 5 mm, in steps of 0.5 mm, in order to provide as a good comparison with coins having the same thickness.

Results

The geometry of the samples plays a decisive role in the quantitative XRF: Fig. 3 shows that the X-ray beam or electron beam may have a different incident angle, Φ_{inc}, penetrating in a convex surface: a) at high incident angles (with respect to the normal direction) the ionized layers are close to surface so that the self- absorption effects of the X-ray emission are negligible; b) for small incident angle the

ionized layers are depth and the self-sorption effects appear to be more consistent.
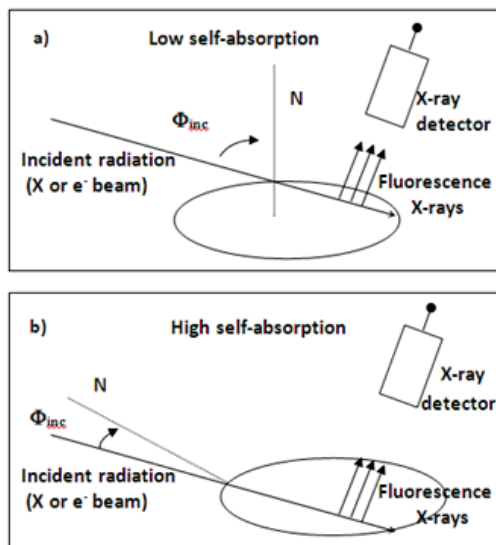

Fig. 3. Sketch of geometry for a) low self- absorption effects and for b) high self-absorption effects.

As a matter of fact, when the surface morphology has convexities, the study of geometry, concerning irradiation, X-ray detection and the region of the analyzed surface is crucial.

In order to take into account the X-ray yield vs. target irregularities, we studied the dependence of the Ag-L$_\alpha$ line X-ray yield on the incident angle for a convex surface having 1 cm curvature radius. As results show (see Fig. 4a), at large angles (glancing conditions) the yield increases, while it decreases at low incidence angles (close to the normal incidence).

A gradient of about 60% may occur due to these geometrical effects with the consequence of altering the final results of the Ag concentration measurements. So, the best choice - when possible - is to analyze the flat regions of the coins; in other cases, one needs to correct the quantitative yield for the 'corrective factor' due to the self-absorption effect. The metal thickness deserves a particular care too, since the Ag-L$_\alpha$ yield, induced by 23 keV X-rays, linearly increases with the film thickness up to about 2.5 mm

thickness (saturation value), as reported in the plot of Fig. 4b. A lower thickness of the coins can affect the total Ag-yield due to a lower X-ray fluorescent yield emitted by the sample. Thus the comparison between the standard thickness and the coin thickness must be considered in order to have a correct quantitative determination of the Ag content. As an example, Fig. 5 shows a typical XRF spectrum obtained analyzing an old silver coin: Greek Drachma, IV Cent. B.C., while Fig. 6 reports a typical XRF spectra obtained analyzing a recent silver coin: 1 Swiss Franc,
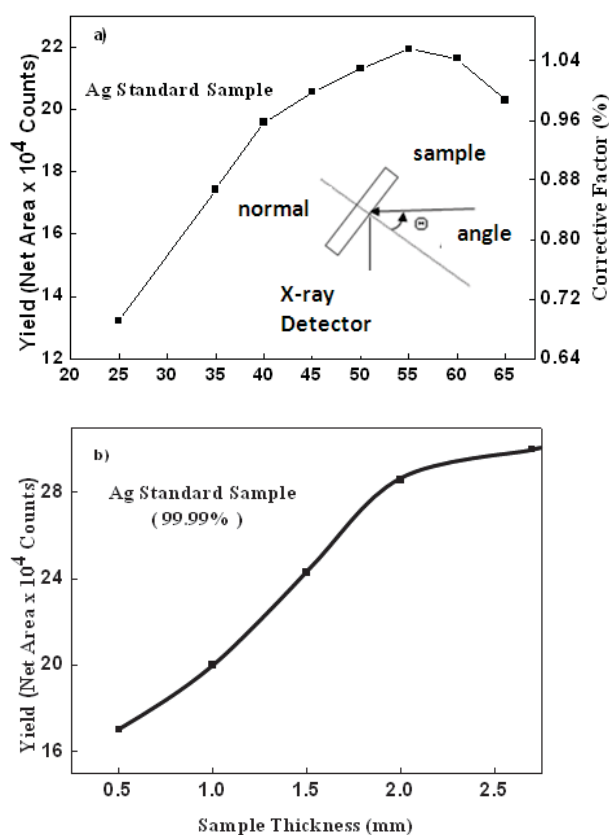

Fig.4. a) Ag-L$_\alpha$ line X-ray yield vs. the incident angle for a convex surface having 1 cm curvature radius and b) the plot of Ag-L$_\alpha$ yield vs. the film thickness.

1934. In our investigations, the quantitative analyses are based on the comparison with the standard sample as follows. The X-rays yield is described by the relation:

$$Y = C \, \phi \, \varepsilon \, \sigma_p \, \Delta t \, F_c \qquad (1)$$

where C is the element concentration, ϕ is the radiation flux (X-rays or electrons), ε is the detection efficiency, σ_p is the X-ray production cross section for the given line, Δt is the collection time and F_c is the corrective factor with respect to the flat surface of the standard. Operating in the same experimental conditions of analysis for coin and standard, the measured concentration in the coin is given by:

$$C_c = C_s Y_c / Y_s F_c \qquad (2)$$

The elemental atomic composition was measured for the bulk and for the surface patina by using the X-ray tube excitation and the electron SEM microbeam probe, respectively. The bulk analysis is reported in the upper spectrum while the surface analysis is featured in the bottom one (see Figs. 5) and 6). Taking into account the amount of Ag in the bulk of the coin, the measurements were performed with respect to the standard sample of pure Ag, with the same thickness of the analyzed sample.
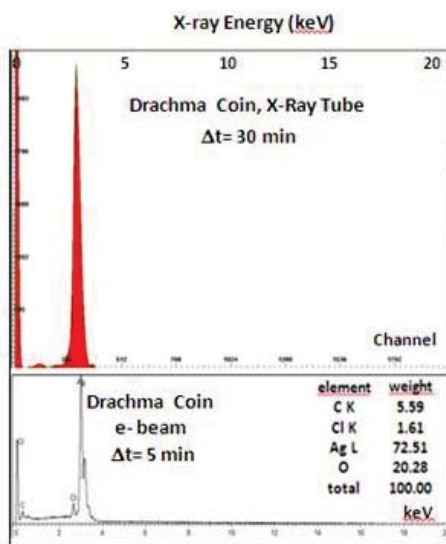

Fig.5. Set of a typical XRF spectra obtained analyzing the old silver coins: #1.

The Ag content of the bulk is always larger than the value measured in the patina layers mainly due to the presence of layers containing silver oxide. As Table I clearly

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shows, the patina contains from about 5% to about 50% less than the percentage of Ag in the bulk. This result can be attributed to contamination and to oxidation processes occurring on the coin surface. The most of superficial layers are composed by Ag_2O and CuO and contain many oxidized species, such as MgO, CO_2, SiO_2 and SO. All coins show an amount of Cu, as contaminant or as high content of the bulk composition. Cu is present as traces, as for the coin #3 and #4, where its atomic concentration is 0.33 and 0.13%, respectively. Cu is present as a bulk contribution below 10%, such as for the coins #1, #2, #6 and #8, some times at higher concentrations, such as for the coins #5, #7, #9 and #10. In coin surface the Cu content is lower with respect to its content in the bulk, again due to the presence of oxidized species at the surface, such as CuO and Cu_2O.
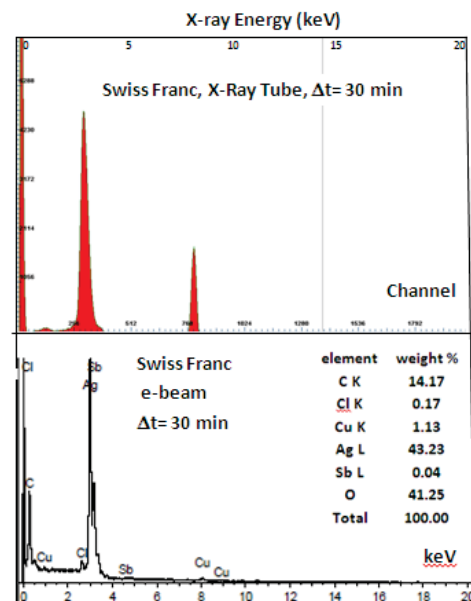

Fig.6. Set of a typical XRF spectra obtained analyzing the recent silver coins: #6 (a)

The evaluation of the thickness of patina coating in recent and old silver coins should be useful to distinguish between true and false coins, in order to find the best methodology to preserve the maintenance of coins inside museums, as well as for historical classifications and forensic

investigations. These measurements have been performed in order to improve the technique, to evaluate the correct element concentration measurement and to assure the repeatability of the analyses.

Coin	#1 Greek Tetradrachm - Messana, 470-466 B.C.	#2 Greek Tetradrachm- Messana, 470-466 B.C., (counterfeit)	#3 Roman Denarius, II cen. B. C.	#4 Drachma, IV cen. A.C.	#5 Gigliato R. D'Angiò, XIV cen. A.C. (counterfeit)	#6 1 Swiss Franc, 1934	#7 Quarter Dollar, 1943	#8 5 Lire, V. Emanuele II, 1945	#9 500 Lire, G. Marconi, 1974	#10 500 Lire, Caravelle, 1960
Weight (g)	17.50	18.00	3.60	3.81	3.60	4.96	6.11	4.90	11.00	10.83
(E) Ag content (atm %)			73.00--89.00	90.00			90.00	83.50	83.50	83.50
(M) Ag-bulk content (%)	74.40	83.30	89.00	73.00	35.00	82.60	82.50	75.00	69.00	83.00
(M) Ag-patina content (%)	63.70	71.25	76.38	72.51	23.35	57.44	75.29	70.33	60.00	73.32
(E) Cu content (%)						5.00	10.00	4.00	16.50	4.00
(M) Cu content (%)	1.00	2.50	0.33	0.13	33.40	6.45	13.00	5.00	13.80	13.60
Bulk Ag content errors (%)			11.00--8.90	16.60			8.30	1.30	17.30	1.16

Table I. Percentage of silver and copper evaluated inside and on the surface of old and recent coins and their comparison with expected values; (E)=expected, (M)=measured.

Finally, XRF analysis is an useful technique to study the Ag content in bulk and patina surface. Other analyses should be considered in order of course to confirm our results and to have other characterization of the coins. Chemical investigation, X-ray diffraction, depth profiles analyses and others should be apply as comparative and complementary techniques to XRF in order to obtain more coin bulk and surface characterizations [9, 10].

Discussion and conclusions

Analyses already presented in literature [9] are in good agreement and often show that oxygen in the ratio Ag/O is low in recent coins; on the contrary, it should be higher in old coins. This trend validates that patina coating is thinner in recent coins and seems to reach tens of microns; on the other hand, in older coins it is thicker, growing up to hundreds of microns.

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