Microchemical Journal 144 (2019) 309–318

Contents lists available at ScienceDirect

Microchemical Journal

journal homepage: www.elsevier.com/locate/microc

New insights on medieval *Provisini* silver coins by a combination of non-destructive and micro-invasive techniques

Melania Di Fazio[a], Francesca Di Turo[a], Laura Medeghini[a], Lucilla Fabrizi[a], Fiorenzo Catalli[b], Caterina De Vito[a,*]

[a] Department of Earth Sciences, Sapienza University of Rome, P.le Aldo Moro 5, Rome, Italy
[b] Via Attilio Friggeri 95, 00136 Rome, Italy

ARTICLE INFO

Keywords:
Provisino
Cu-Ag coin
XRD, SEM, EIS, VIMP, techniques
μ-Raman
Corrosion products

ABSTRACT

The aim of this research was to characterize ten *Provisini*, one of the most common silver coins in the Middle Age, dating back to the 13th century A.D. These coins are composed by Ag-Cu alloy and were coined in the Roman mint. A non-destructive, micro-destructive and multi-analytical approach was used, aiming to preserve the surfaces of the coins. The results of XRD and micro-Raman spectroscopy allow defining the alloy composition and the mineralogical nature of the alteration products (e.g. cuprite, tenorite, chlorargyrite, stromeyerite). X-ray maps provided information on major elements distribution on the surface. Finally, Electrochemical Impedance Spectroscopy (EIS) and Voltammetry of Immobilized Micro-Particles (VIMP) permitted to reconstruct the possible scheme of the multi-layering of the *patina* on the coins. Then, the conservation status was monitored.

1. Introduction

The study of ancient metal artefacts has provided information about technological production as well as the materials that were used, permitting to explore the provenance of the raw materials involved in their production [1–4]. In addition, important technological insights are given by means of systematic chemical and microstructural analysis, which revealed information about the technological background available for processing materials [5–8].

Various analytical techniques have been extensively used in the study of ancient coins, providing useful physic-chemical features. For example, optical microscopy and scanning electron microscopy (SEM) were used to investigate the surfaces morphology, the signs of coinage and the corrosion products [9,10]. The application of X-ray diffraction (XRD) [10,11] and μ-Raman spectroscopy [6,12–15] helped to determinate the mineralogical nature of the alteration products. Electrochemical techniques, i.e., EIS (Electrochemical Impedance Spectroscopy) and VIMP (Voltammetry of Immobilized Micro-Particles), were fundamental to study corrosive products [16–20], caused by environmental degradation, and to date archaeological samples [21–24].

One of the main features of ancient silver coins is related to the presence of silver surface enrichment, probably due to segregation of the metals during casting or cooling, mechanical treatment or abrasion and corrosion processes [5].Indeed, the concentrations of Ag and Cu and other minor elements (e.g., Sn, Zn, Pb, Fe), determined in different ways, cannot reflect the real composition of the alloy that is not homogenously distributed in the surface due to enrichment phenomena [25,26].

The aim of this research is to characterize the alloy composition of ten medieval coins named *Provisini*, minted during the 13th century CE. With this aim, XRD analysis and micro-Raman spectroscopy were applied to determine the mineralogical composition of the alteration of the patina. SEM, semi-quantitative analysis and X-ray maps of elements were applied for morphological characterization of the surfaces and to have information about the chemical composition. These coins were also studied employing two electrochemical techniques, *i.e.* Voltammetry of Microparticles (VIMP) and Electrochemical Impedance Spectroscopy (EIS). VIMP is a technique developed by Scholz et al. [27,28] for studying the electrochemistry of minerals and then refined and extensively applied by Doménech-Carbò et al. in conservation and archaeometric fields [4,22,24,29–33]. This technique allows obtaining an electrochemical fingerprint of the *patina* composition thanks to the voltammetric peaks of each compound on it. On the other hand, EIS was used for monitoring of the corrosion processes and testing the protective coatings, aiming to the conservation of metals [19,34–38]. More recently, EIS has been considered a valuable tool also to discriminate coins for provenance and/or dating [19,21,24]. Here, VIMP and EIS are used to characterize the surface composition of the coins, evaluating

* Corresponding author.
E-mail address: caterina.devito@uniroma1.it (C. De Vito).

https://doi.org/10.1016/j.microc.2018.09.016
Received 23 July 2018; Received in revised form 14 September 2018; Accepted 15 September 2018
Available online 19 September 2018
0026-265X/

also the condition of conservation along with the techniques cited above.

These results can contribute to fill the existing gap on the Italian medieval *Provisini* and to improve the knowledge on ancient silver alloys.

2. Historical context

The *Provisino*, a medieval coin made of a silver-based alloy, was the first denomination minted by the *Senatus Romanus* in 1176–1177 CE, after the reopening of the Roman mint. It was exclusively produced by the mint of Rome during the first seventyyears of its activity [39]. It represented an imitation of the *Provinois*, a French silver rich coin, which the name derived from Provins city (dept. of Seine and Marne, France), where its coinage started.

This original French coin was minted from the Counts of Champagne since the first half of 12th century (with the *Count Thibaud II*, 1125–1152 CE) until the second half of 13th century (with the *Counts Henri I*, 1152–1180 CE and *Henri II*, 1180–1197 CE) [40]. All these denarius show on the obverse a legend with the name of the reigning Count and on the reverse the legend "CASTRI PRYYNS", with the image of a wool comb (the word Champagne comes from the French "champ-peigne", comb in a camp) [41].

In the 12th centuryCE,the absence of a local currency in the South Reigns of Italy and the good intrinsic value of the French*Provinois* favoured thecirculation of this nomination also in the Roman area [42,43].

Usually, the *Provisino of the Senatus Romanus* presents on the obverse the legend "ROMA CAPVT MV (*ndi*)", the image of the wool comb and an "S" on the head of the comb, whereas on the reverse is reported the legend "SENATVS P.Q.R." and a cross rounded by symbols that imitate the alpha and the omega typycal of the Champagne coins. Furthermore, the oldest coins are characterize by an irregular shape [40]. They will become more accurate, with a clear coinage, from the half of the 13th century to the end of the 14th century (the last period of emission of provision coins).

For medieval people the *Provisino* was a common coin of low value and for daily purchases, becoming in few years the reference currency for all monetary exchanges in Rome.

The Roman *Senatus* continued to mint *Provisino* for about 200 years, with the only exceptions of the coins minted by Cola Di Rienzo in 1347 CE, Pope Boniface VIII in 1398 CE and other few coins minted by the *Senatus* and authority of Pope. Some documents dating back to 13th–14th centuries, from religious archives, talk about the *Provisino* as a currency for the payment of tithes [40]. Pope Innocent III imposed in his lands, with a papal bull in 1208 CE, the exclusive use of *Provisino* as the only currency, with an exchange of 16 Roman coins for 12 French ones [41].

The different emissions of *Provisino* changed in shape, weight and value, until the monetary reform imposed in 1439 CE by Pope Eugene IV (1431–1447), that ended gradually the coinage by *Senatus Romanus* in favour of the pontifical ones [44,45].

3. Material and methods

3.1. Materials

A set of 10 coins (named from 1F to 10F) were selected from a private collection (Fig. 1). Numismatic examination of these coins identified all samples as *Provisini*, which were minted in 13th century A.D. in Rome by the *Senatus Romanus*.

All coins have a cross surrounded by a circular legend on one side; some specimens have, on the second side, the same cross and a circular legend, whereas other samples have the image of a wool comb, the characteristic image of the French Provinois minted in the 12th–13th centuries CE.

The weight of the studied samples varies from 0.33 g to 0.81 g and their diameter from 12 mm to 18 mm. The irregular shape of the coins is typical of the first minted *Provisini* [40], which can be justified with both the wear of time and the medieval "*tosatura*" technique,a common practice for recovering precious metals [46].

3.2. Methods

Micro and non-destructive and non-invasive methods are applied to characterize the *Provisini*. XRD analysis was performed by means of Siemens D5000 automatic powder diffractometer, Bragg- Brentano $\vartheta/2\vartheta$ geometry (Department of Earth Sciences, Sapienza University of Rome, Italy). The scanning range was from 5° to 90°, with a scanning speed of 0.03°/1.5 s and XRD patterns are acquired directly on the surface of the samples without consumption of material. Both sides of each coin were scanned. XRD patterns were edited using low smoothing treatment to improve background definition, with the help of XPowder12 software combined with PDF2 database of ICCD.

Raman spectra were acquired using a Jobin-Yvon Horiba LabRam micro-Raman spectrometer equipped with Olympus microscope (10×, 50× and 100× optical lenses) and He-NE 632.8 nm laser (Department of Physics and Earth Sciences, University of Parma, Italy). Exposure time for spectra acquisition was between 30 and 100 s, from 1 to 3 repetitions. 20 points for each sample were analysed, considering the inhomogeneity of the patina. Data were interpreted by RRUFF database and Parma University database (http://www.fis.unipr.it/phevix/ramandb.php). LabSpec software v. 5.58.25 was used to process data.

SEM-EDAX data were performed using a FEI Quanta 400 instrument with an EDAX Genesis Microanalysis system (Department of Earth Sciences, Sapienza University of Rome, Italy). SEM imaging analysis, i.e., SE (secondary electrons) and BSE (back-scattered electrons), was carried out to investigate the morphology of the coin surfaces, whereas EDS spectra permitted to acquire chemical composition of the first 5–10 μm in depth. The points analysed at high magnification were selected, after a low magnification investigation, based on the chemical composition and the morphology of the patina. X-ray maps showed the elemental distribution on the surfaces.

VIMP studies were performed employed commercial graphite bar (Staedtler Mars 200 HB, 2.0 mm diameter) as working electrode dipped into a 0.10 M $HClO_4$ aqueous solution as supporting electrolyte, as widely described in literature [22,23,29,47]. "One touch" methodology [48] was applied on three points for each coin, selected on the bases of the homogeneity or the inhomogeneity of the patina. The potential scan was initiated at +0.75 V in the negative direction. The potential step increment was 4 mV, the SW amplitude was 25 mV and the frequency 5 Hz. A standard three-electrode arrangement was used with a carbon auxiliary electrode and a SCE (Saturated calomel electrode) as reference electrode.

EIS measurements were realized with a modified electrochemical cell, to permit the partial immersion of the coin into mineral water (composition: NO_3^- < 0,5 mg/l, NH_4^+ < 0,05 mg/l, Na^+ = 57 mg/l, K^+ = 1,7 mg/l, Ka^{2+} = 33 mg/l, Mg^{2+} = 17 mg/l, F^- = 0,2 mg/l, Cl^- = 42 mg/l, SO_4^{2-} = 24 mg/l, HCO_3^- = 233 mg/l, SiO_2 = 12 mg/l) as already described [22]. SCE allowed setting up a traditional three-electrode arrangement using the coin under study as working electrode. Spectra acquisition was realized in 0.1 Hz–100,000 Hz frequency range, with 10 mV amplitude at the Open Circuit Potential (OCP). Then, EIS spectra were fitted with the more appropriate Equivalent Circuit (EC).

For each coin, three different EIS measurements were carried out for the reproducibility of the analysis.