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Elemental characterization of surface and bulk of copper-based coins from the Byzantine-period by means of spectroscopic techniques

Matteo Crosera¹, Elena Baracchini¹, Enrico Prenesti², Alessandro Giacomello³, Bruno Callegher⁴, Paolo Oliveri⁵, Gianpiero Adami^{1*}

- ¹ Dipartimento di Scienze Chimiche e Farmaceutiche, Università degli Studi di Trieste, Via Licio Giorgieri, 1 34127, Trieste (Italy)
- ² Dipartimento di Chimica, Università degli Studi di Torino, Via Pietro Giuria, 5 10125, Torino (Italy)
- ³ Regione Autonoma Friuli Venezia Giulia ERPAC, Villa Manin, Piazzale Manin, 10 33033, Passariano, Udine (Italy)
- ⁴ Dipartimento di Studi Umanistici, Università degli Studi di Trieste, Via Lazzaretto Vecchio 8 34124, Trieste (Italy)
- ⁵Dipartimento di Farmacia, Università degli Studi di Genova, Viale Cembrano, 4 16148 Genova (Italy)

* Corresponding author: Gianpiero Adami, gadami@units.it

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Abstract

Thirty-three Byzantine copper-based coins (so-called anonymous *follis*) from 970 to 1085 A.D. were investigated in order to determine the elemental composition both of the bulk and of the surface. The ancient coins analysed – belonging to the Thomas Bertelè Collection, now located in the Bottacin Museum of Padova (Italy) – were studied by way of physical, chemical and chemometric testing techniques. This study aims to obtain information on socio-economic aspects of the Byzantine Empire using chemical and physical data of currency as indirect indicators. First, the weight, diameter and thickness of each piece were measured, then a micro-Energy Dispersive X-Ray Fluorescence (µ-EDXRF) technique was applied on a cleaned and polished area of the surface of the coin to evaluate the presence of minor elements in a non-destructive fashion. A micro-destructive sampling method for both surface and bulk samples, based on mechanically drilling the edge, was finally employed, and Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) was used for the quantitative

determination of Cu (the major alloying element), Pb, As, Fe, Zn, Ag, Ni, Sn and Mn (minor elements) in the powder which resulted from drilling each coin, previously dissolved *via* aqua regia dissolution technique overnight at room temperature.

The average copper concentration of the *folles* was $95.9\pm3.1\%$ for the bulk and $91.7\pm3.5\%$ for the surface. The Pb-Cu ratio appears to be an index which can be used to discriminate between different coins, in particular for Class B (from 1030 to 1042 A.D.), as confirmed by exploratory chemometric data analysis. According to our results, all the anonymous Byzantine *folles* under examination were minted in much the same way and using the same mineral raw materials. Using the chemical data measured on the bulk, we can grasp that the monetary choice of the period under study excluded silver, gold and bronze (concentrations of Pb is low, while Sn resulted undetectable or unquantifiable) to turn, substantially, to a copper-only coinage (deducted the impurities given by the gangue of the starting minerals). Moreover, along the observed period of 120 years, the mass of the coins was significantly reduced (with an overall loss of material of approximately 60%).

1. Introduction

1.1. Historical background

Coins can provide valuable information regarding various aspects of ancient civilizations that used them. This study aims to obtain information on socio-economic aspects of the Byzantine Empire in the 11th century using chemical and physical data of currency as indirect indicators. The Byzantine Empire saw a remarkable economic change between 820 and 1204 A.D.. One of the most significant changes was the interruption in the minting of the *miliarense* (a silver coin) due to a lack of silver. As a consequence, the currency supply was provided by a new *follis* (copper coin) type. First, John I Zemisces ordered that the portrait of Christ, which had previously been stamped only on gold coins, would also be represented on *folles*. Secondly, the *folles* were not coined in the name of a particular emperor and for this reason they have been defined as *anonymous*. In most cases, the obverse of the coin (recto) features the image of Christ with the following inscription on the reverse (verso): +IhSqS XRISTqS bASILeq 'bASILe' which translates as "Jesus Christ King of Kings".

The origin of these coins is known *via* literary sources and can therefore be fixed as being produced during the reign of John Zemisces. The anonymous *folles* are grouped into 15 classes, from A to N according to the variety of coins. In this work, the Classes A to J are examined (approx. 970 – ca. 1085). Sources, in particular the "Palaia kai Nea Logarikē", suggest the persistence in the taxation of the old gold/silver/copper exchange ratio: 1 *nomisma* = 12 *miliarenses* = 288 *folles*. However, it should be noted that the first standard weight of the *follis* of 13 g (Class A1), shortly afterwards

increased up to 18 g (Class A2), and then it went back to the previous standard (Class B). This weight, nonetheless, declined progressively to 7-8 g in the last part of the 11th century, but also reached 5 g in the final coinage of this copper series (Classes I-J). The effects of these weight differences are still a matter of debate, since it is unclear if they affected the system of accounting and the exchange rate with precious metal coins. There were also alterations of the alloy that merit further investigation in order to clarify if this alteration impacted the value of the fiduciary *follis* and, if so, to what extent. In fact, it can be hypothesized that the variation of the price of the raw metal on the market may have had an impact on the circulating value of the *follis*. This should be noted both in relation to its value during its period of use with regard to the *miliarense*, as a unit of account, and the same concerning the *nomisma*. This variation in the mass and composition of the *folles* [1-5].

1.2 Chemical analysis

Physical and chemical measurements on ancient coins provides information on the metals used (native or extracted from a metal ore, mainly oxides or sulphides) and, indirectly, on the economy of the period in which they were minted. The metals used, in turn, provide insight into the civilization under study and on its i) technological skill, ii) availability of mineral raw materials, and iii) economic stability. In particular, by monitoring the physical and chemical features and all the coins' characteristics over a protracted period, it is also possible to verify the devaluation process which consists of the increasing use of less noble metals in the coinage process (modifications made to alloy composition), rather than in using smaller coins, with respect to the past, having the same nominal value on the market.

Because of the uniqueness and the great historical value of these items [6,7], the analyses should be non-destructive, although most of the non-destructive techniques act only on the surface of the material analysed and destructive techniques often provide more reliable compositional information for both the bulk and the surface. The most commonly used non-destructive techniques for elemental determination are: μ -EDXRF (micro-Energy Dispersive X-Ray Fluorescence, henceforth μ -XRF) spectroscopy, Neutron Activation Analysis (NAA) and the X-Ray emission induced by particles (PIXE). The μ -XRF technique is generally used in semi-quantitative analysis, since, in most cases, the samples analysed are not homogeneous enough to obtain quantitative results. The homogeneity of the surface and the presence of at least a small flat surface are necessary conditions for this kind of investigation [8].

Degradation compounds of some metallic elements very often appear on the coins' surface. Particularly, copper is a relatively reactive element; generally, its reactivity regards only the surface, unless SO₃ or chloride ion are present, which have the ability to cause deep chemical corrosion up to the formation of copper(II) hydro soluble compounds. Hence, analyses must be planned taking into account the surface alteration of the composition of the alloy, due to corrosion caused by oxidizing substances found in the natural environment and complexing agents able to form stable Cu(I) or Cu(II) compounds [9, 10].

Recent studies [11] were conducted on Austrian "*Tiroler Kreuzer*" medieval coins consisting of an Ag-Cu alloy. The surface of these coins showed the typical green patina arising from the oxidation of copper. The surface composition was determined *via* μ -XRF spectroscopy, while the cross section was examined by SEM-EDX (Scanning Electron Microscopy coupled with Energy Dispersive X-Ray analysis). A comparison with the bulk composition showed a depletion of copper and an enrichment in silver in the surface layer. The results revealed a difference of more than 50% between the bulk and surface composition.

Recent literature on archaeological coins is rich in papers dealing with silver and silver/copper alloy in historical coinage process [12-19].

In this paper, resulting from a collaboration of various public research bodies, thirty-three anonymous Byzantine copper-based coins (*folles*) from the XI century (from 970 to 1085 A.D.) – belonging to the Tommaso Bertelè Collection, now located in the Bottacin Museum in Padova (housed within the Eremitani Museum complex in Padova, Italy) – were studied by way of physical, chemical and chemometric testing techniques. First, the weight, diameter and thickness of each piece were determined. Then, μ -XRF, a non-destructive technique, was used to identify the alloy elements on the surface of the coins (Cu, Pb, As, Fe, Zn, Ag, Ni, Ca, K, Si, Ti), as already indicated by the specific literature [20-21]. A micro-destructive sampling method – based on mechanically drilling the edge of each coin [22] – was then used and subsequently, Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), a destructive technique, was employed in the determination of Cu (a major alloying element), Pb, As, Fe, Zn, Ag, Ni, Sn and Mn (minor elements, lower than 10%) in the powder resulting from the drilling of each coin (both from the bulk and the surface) previously dissolved *via* aqua regia attack overnight at room temperature

Besides the strict chemical characterization, the aim of this study includes the possible identification of groups of coins from different coinage periods demonstrating particular and historically significant features. These data should be considered input for the first numismatic database and as the starting point for significant feedback regarding anonymous *folles* from the eleventh century in the area of the Byzantine Empire.

2. Materials and methods

2.1 Chemicals and apparatus

All chemicals used were of analytical grade. Nitric acid ($\geq 69\%$ w/w), hydrochloric acid ($\geq 37\%$ w/w) were purchased from Sigma Aldrich (Milan, Italy). Water reagent grade was produced with a Millipore purification pack system (MilliQ water). Standards of Cu, As, Ni, Pb, Zn, Ag and Fe used for the calibration curves for ICP-AES analyses were obtained by dilution of SPECTRASCAN[®] 1,000 mg/L standard solutions (in 2.5% HNO₃) purchased from Teknolab (Drøbak, Norway).

A Dremel 300 series drill (10,000-30,000 rpm) was used in the sampling procedure with HSS drill bits DIN 388 for iron and metals (diameter 1.0 mm).

The powder resulting from drilling was weighed by means of an electronic weigh scale, Sartorius Research R200D (readability: 0.01 mg; standard deviation ≤ 0.02 mg; stabilization time: 7 s), placed on an anti-vibration table with a granite plate. Diameter and thickness were measured with a Vernier caliper in three places on each coin.

2.2 Studied folles and physical characterization

The 33 examined *folles* were grouped into 11 classes (3 *folles* for each class) as reported in Table 1. The rarest coins belong to Classes E and F, while objects pertaining to Class A were subdivided into A1 and A2 (found mainly in Germany and France), due to both a great variety of ornamentation (decorations of the halo and the Gospel) and a significant difference in weight.

Specific dimensional and mass characteristics of the coins are also indicated in Table 1.

In Figure 1, 4 *folles* belonging to Classes A2, B, C and J are shown.

2.3 µ-XRF qualitative measurements

Micro-Energy Dispersive X-Ray Fluorescence Spectrometry (μ -EDXRF) was initially employed to identify the presence of elements other than copper. This technique is useful to gather information relative to surface composition since only low depths can be reached. On the other hand, no treatment of the sample was required. Measurements were performed on the cleaned and polished area of each coin surface.

The elemental analysis was carried out by an ARTAX 200 micro-XRF spectrometer (supplied by Bruker Nano GmbH). The instrument consists of an air-cooled Mo X-ray fine focus tube (max 50 kV, 1 mA, 40 W) controlled by a compact high voltage generator unit and equipped with a 650 mm collimator. It is equipped with a Peltier cooled XFlash® silicon drift detector (10 mm² of active area and energy resolution <150 eV for Mn–Ka at 100 kcps) and a colour CCD camera (500 × 582

pixels) for sample positioning. The focal spot is $1.2 \times 0.1 \text{ mm}^2$ with a 0.2 mm lateral resolution and a 100 µm beryllium window.

The ARTAX control semi-quantitative XRF software was used for hardware control and analytical data evaluation. Data are plotted as counts versus energy (keV). For our analyses, the instrument was set up with the following test parameters: X-ray tube = 30 W, Mo target U = 50 kV, I = 700 μ A, acquisition time = 60 s (live time), collimator = 650 μ m (air environment).

The examined elements were: Cu (line: K α 1 8.0463 keV), Pb (line: L α 1 10.551 keV), As (line: K α 1 10.5434 keV), Fe (line: K α 1 6.4052 keV), Zn (line: K α 2 8.6141 keV), Ag (line: K α 2 21.99 keV), Ni (line: K α 1 7.4803 keV), Sn (line: L α 1 3.4441 keV) and Mn (line: K α 1 5.9003 keV)

2.4 Micro-destructive surface/bulk sampling technique and sample preparation

Sampling was carried out using a mechanical drill equipped with a tungsten-carbide drill bit (1 mm diameter at 20,000 rpm). Drilling started at the edge and extended on a radius to a depth of approximately 0.5 mm (see Figure 2).

This first sampling powder (at least approximately 3 mg) constituted the surface sample (henceforth referred to as S). In a second step, drilling continued until a depth of about 3 mm. This sampling powder (about 10 mg) constituted the bulk sample (henceforth referred to as B).

The powder obtained was collected in boxes constructed from greaseproof paper, 2 cm x 2 cm, well folded in such a way as to facilitate subsequent transfer. It was decided to use greaseproof paper cards after noticing that, due to electrostatic phenomena, the metal powder tended to adhere less to this type of support. Cards had to be handled with nitrile gloves.

Both powder samples were carefully weighed by means of the semi-micro scales, dissolved in aqua regia $(1:3 \text{ v/v}, \text{ concentrated HNO}_3: \text{HCl} \text{ aqueous solution})$ overnight at room temperature and diluted in a 10 ml calibrated flask (Class A) with MilliQ water (Nir-EI, 2009).

2.5 ICP-AES analyses

Sample solutions were analysed *via* ICP-AES spectrometer (Spectroflame Modula EOP, Spectro). The limit of detection (LOD) in the solution sample at the operative wavelength for each element was: 0.025 mg/L for Cu at 324.754 nm, 0.050 mg/L for Ag at 328.068 nm, 0.050 mg/L for As at 188.979 nm, 0.050 mg/L for Fe at 259.940 nm, 0.050 mg/L for Ni at 231.604 nm and 0.050 mg/L for Pb at 220.353 nm. The repeatability of the measurements as relative standard deviation (RSD%) was always lower than 5%. Sn and Mn were also examined, although their concentrations were found to be below the LOD of the method used (0.050 mg/L in solution, corresponding to 0.01% in the *folles*).

Repeatability was also calculated on the same *folles* conducting 5 replicates on one real sample, repeating the entire analytical procedure including micro-destructive sampling. The RSD% values were always lower than 5% for all the examined elements.

The accuracy of the measurements was only calculated for copper by means of a simulated standard copper coin obtained by a copper foil of 99.9% title in copper (thickness 2 mm, by Sigma Aldrich); recoveries were always greater than 95%.

2.6 Data processing

Mean data (physical and chemical measurements averaged according to the age class) were submitted to bivariate analysis by computation of Pearson's correlation coefficients between couples of variables. Computations were performed using MS-Excel (Microsoft Corporation, Redmond, WA, USA, Version 2013).

The same data were then submitted to an unsupervised multivariate exploratory approach, by means of Principal Component Analysis (henceforth: PCA). Considering the heterogeneity of the physical and chemical variables under study, as well as their very different measurement units, data were preliminarily pre-processed by column auto-scaling.

PCA outcomes were evaluated graphically by examination of the resulting biplot, in which scores (projections of samples in the PC space) and loadings (contributions of original variables to the definition of the PC space) were superimposed. Examination of this plot allows one to comprehensively understand trends and patterns within samples, inter-correlation among variables, and relationships between samples and variables [23].

Multivariate data processing was performed by means of in-house Matlab routines (The MathWorks, Inc., Natick, USA, version 2018a).

3. Results and discussion

3.1 μ -XRF qualitative results

The preliminary qualitative analysis of all the *folles* was performed using μ -XRF and allowed for the identification of the most important elements present in the different samples. In particular, in addition to copper, the largest elements in all the *folles*, Pb, As, Fe, Zn, Ag and Ni, were identified. Sn and Mn did not provide significant μ -XRF signals. The subsequent ICP-AES micro-destructive analysis was addressed mainly to these elements.

3.2 ICP-AES quantitative results and discussion

The calculated concentrations in percentage both for bulk (B) and surface (S) samples are reported in Table 2. We report the average value of concentration calculated on 3 *folles* (for each class) and the corresponding standard deviations. Considering all the *folles*, the average copper concentration was $95.9\pm3.1\%$ for B samples and $91.7\pm3.5\%$ for S samples. We found Sn and Mn concentrations always lower than 0.05%, as already foreseeable by the μ -XRF results.

Surface loss of copper can be easily explained considering the formation of alteration compounds (copper is on the short list of noble metals by many chemists, although its resistance to oxidation is limited with respect to Ag and Au of the same group 11), due to the interaction of the metal material with natural oxidizing environmental agents (mainly forming oxides, hydroxides, sulphurs, sulphates, carbonates and chlorides). These interactions are also well described by Inberg et al. [19].

As to the elemental composition of the coins' bulk, we can observe the low percentage of Pb (always < 1.5%) and the noteworthy absence of Sn (always undetectable or unquantifiable): this allow one to exclude that it was the intent of the smelters to specifically manufacture a bronze alloy, characterized by the presence of tin and/or lead (arsenic is a component of very old type of bronze, here As is always < 1%). We can therefore see that the monetary choice of the period under study excluded silver, gold and bronze, turning to a copper-only coinage (apart from the impurities found as a result of the gangue from the raw minerals). This change of metals used to coin coins may denote economic instability, with lowering the standard of living by a crisis, or a temporary tendency in the economization of raw materials (for socio-political difficulties in businesses and so on).

For each class, we calculated the ratio between the minor element and the copper concentration. Some *folles*, in particular those from Class B, showed significantly different Pb/Cu and Zn/Cu ratios, likely depending upon their coinage period. Moreover, the B-group *folles* presented the lowest percentage of copper but with a high standard deviation. These *folles* show a decrease in copper content, but not in size. After the year 1042, it was likely decided to reduce the size of the coins while maintaining the previous composition (Classes A1 and A2) copper content.

Coins from Classes B and E demonstrated a lower percentage of copper than of the other elements. Pb concentration was higher, as in the other classes, while the presence of elements such as Ca, K, Si and Ti (identified by way of μ -XRF) could provide an explanation as to why the levels of copper were lower in these coins (it is possible that raw mineral materials from different geographical origins were used in that historical period, or a different pyro-metallurgic technique – such as a particular purification method from the gangue – was employed).

The Cu percentage remained fairly constant over time, with the previously mentioned exceptions, but a decrease in the weight and thickness of each coin was quite evident.

In particular, calculating the total mass of copper in the coins from the single classes, one can note the regular decreasing trend (see Figure 3), particularly starting by Class A2 (976-1030/35 A.D.). The overall loss of mass is of approximately 60%.

3.3 Correlation matrix and chemometric analysis of data

We can use the bulk data of metals to calculate the correlation matrix to identify positive or negative correlations. We noted negative correlations between diameter (thickness and weight) and the year of coinage, while significant positive correlations were observed between Zn, Ag and Pb, as shown in Table 3.

PCA was performed on physical and chemical data averaged for classes of age, after column autoscaling, in order to reveal temporal trends – or different grouping patterns – within the scores, and relations among variables within the loadings.

From an examination of the biplot (Figure 4), one can clearly note that PC1 is mainly associated with a temporal trend; in fact, the oldest samples (colored in blue) are mainly found on the left part of the plot (at the lowest PC1 score values), while the most recent samples (colored in red) are found to have the highest PC1 score values.

A quite regular trend – with a few irregularities – can be observed for intermediate samples between these two extremes along PC1.

A joint examination of scores and loadings led to the conclusion that the oldest samples were characterized by the highest values of the physical parameters (diameter, thickness and weight) and of total Cu content (all of them characterized by a negative loading on PC1), while all of these parameters underwent a decrease over time. This confirms that along the observed period (120 years from 970 to 1085 A.D.), as previously demonstrated, the coins' mass was significantly reduced and a decrease in the absolute mass of copper was observed, as previously discussed. This could indicate a possible devaluation process in that particular society.

An opposing trend, with respect to time can be seen for variables at positive loading values on PC1, mainly Ni.

Concerning inter-correlation among variables, from an evaluation of loadings it can be concluded that a positive correlation exists among diameter, thickness, weight and total Cu. A second group of positively inter-correlated variables is constituted by Ni, Cu, Fe and As. Interestingly, these two groups of variables – which are the most important in defining the temporal trend along PC1 – were negatively correlated one with respect to the other. A third group of variables, characterized by a slight positive inter-correlation, is formed by Pb, Ag and Zn. These three variables are nearly uncorrelated with the other parameters, being found in an almost orthogonal direction in the PC1 versus PC2 plane.

PC2 mainly explains the differentiation of coin samples characterized by a high Ag, Pb and Zn content. In particular, by a joint analysis of scores and loadings on PC2, it is possible to confirm that samples from Class B present the highest content of Ag and Pb, while samples from Class I present the highest Zn content.

4. Conclusions

The analysis of historical objects of great value requires taking precautions to limit damage. In our study, only a very small portion of the *folles* was removed, up to nearly a depth of a few millimetres. The method proposed, in spite of these limitations mainly due to the scarcity of the sample available, is valid and able to measure the elemental composition (both copper and minor elements) of the coins under study. We optimized a previously used micro-destructive sampling method [22]. We discovered that these *folles* are composed of 96% copper, which is a high percentage if we consider that the *follis* was a fiduciary coin. At the same time, this could confirm the significant presence of copper in the Byzantine Empire during the eleventh century, and especially the large use of copper coins as a means of exchanging gold money into tokens. Among the metals found, tin resulted undetectable or unquantifiable. Coins from the Byzantine Empire left in gold (*solidus* of Justinian II, that became thin wafers that could be bent by hand around 10^{th} century) and were often made in silver (*miliarense*) or in bronze, rather than in almost pure copper (referring to the bulk) as those under study. We can observe that the sunset of the so-called *gold standard* in monetization has a very remote origin.

A decrease in the concentration of copper from the bulk to the surface was also found, compensated for by an increase in the concentration of unidentified elements, since they are present on the surface patina in the form of alteration compounds as oxides, hydroxides or salts.

We attempted to find some relation at the level of elemental composition among the coins belonging to different groups in which they are subdivided. The groups of coins which have a concentration ratio of metal-copper (Pb/Cu and Zn/Cu) above the average, such as group B, will later be subjected to more targeted studies. Group B showed a decrease in the copper content and this could indicate that in order to keep the ratio of exchange fixed with the *follis* of Classes A1 and A2, the percentage of copper in the alloy composition actually decreased.

Such evidence, as well as the historical-based trend, was confirmed by the chemometric exploratory analysis of both physical and chemical properties of the bulk.

The chemical measurements, which cover a period of about 120 years (from 970 to 1085 A.D.), suggest that the most significant variation in the composition is to be found only in Class B, while in all other

classes the percentage remains constant. On the contrary, the weight of the coins changed significantly: it decreased progressively up to three times. This decrease in mass may not automatically indicate a possible devaluation of the face value of the coin itself, because the nominal value of the *follis* would have been maintained in case of a simultaneous increase in the cost of the necessary quantity of copper to be minted. In addition, it should also be underlined that in hoards and excavation findings, the number of *folles* from Class A2-D (the heaviest ones), is much higher than Classes E-J. This appears to exclude a relationship between devaluation and the inflation of the copper currency of this period.

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References

[1] A.E. Laiou, The Economic History of Byzantium. From the Seventh through the Fifteenth Century, Dumbarton Oaks Research Library and Collection, Washington D.C., 2002.

[2] M.F. Hendy, Studies in the Byzantine Monetary Economy c.300-1450, Cambridge University Press, 1985.

[3] A. Bellinger, P. Grierson, Catalogue of Byzantine Coins in the Dumbarton Oaks collection and in the Whittemore Collection, volume 3, part 2. Dumbarton Oaks Research Library and Collection, Washington D.C., 1973.

[4] K. Weber, Prägte Byzanz wirklich schüsselförmige, anonyme Folles? Jahrbuch für Numismatik und Geldgeschichte 50 (2003) 105-109.

[5] C. Morrisson (ed.), Trade and Markets in Byzantium, Washington D.C., 2012.

[6] R. Linke, M. Schreiner, Energy Dispersive X-Ray Fluorescence Analysis and X-Ray Microanalysis of Medieval Silver Coins, Microchim. Acta, 133 (2000) 165-170.

[7] M. Mantler, M. Schreiner, X-Ray Fluorescence Spectrometry in Art and Archaeology, X-Ray Spectrom. 29 (2000) 3–17.

[8] D. M. Metcalf, W. A. Oddy, Metallurgy in numismatics, Royal Numismatic Society, London, (1980).

[9] M.B. Mcneil, B.J. Little, Corrosion Mechanisms for Copper and Silver Objects in Near-Surface Environments, Journal of the American Institute for Conservation 31:3 (1992) 355-366.

[10] H. Mousser, A. Madani, R. Amri, A. Mousser, A. Darchen, Contribution of Microchemical Surface Analysis of Archaeological Artefacts, Physics Procedia 2 (2009) 1249–1254.

[11] R. Linke, M. Schreiner, G. Demortier, M. Alram, Determination of the provenance of medieval silver coins: potential and limitations of X-ray analysis using photons, electrons or protons, X-Ray Spectrom. 32 (2003) 373–380.

[12] O. Abdel-Kareem, A. Al-Zahrani, A. Khedr, M.A Harith, Evaluating the use of laser in analysis and cleaning of the islamic marine archaeological coins excavated from the red sea, Int. J Conserv. Sci. 7 (2016) 511-522.

[13] F.J. Ager, B. Gómez-Tubío, A. Paúl, A. Gómez-Moróne, S. Scrivano, I. Ortega-Feliu, M.A.
Respaldiza, Combining XRF and GRT for the analysis of ancient silver coins, Microchem. J. 126 (2016)
149–154,

[14] A. Lo Giudice, A. Re, D. Angelici, J. Corsi, G. Gariani, M. Zangirolami, E. Ziraldo, Ion Microbeam Analysis in cultural heritage: application to lapis lazuli and ancient coins, ACTA IMEKO 6 (2017) 76-81.

[15] J. Corsi, A. Lo Giudice A. Re A. Agostino, F. Barello, Potentialities of X-ray fluorescence analysis in numismatics: the case study of pre-Roman coins from Cisalpine Gaul; Archaeol. Anthropol. Sci. 10 (2018) 431–438.

[16] J. Corsi, F. Grazzi, A. Lo Giudice, A. Re, A. Scherillo, D. Angelici, S. Allegretti, F. Barello, Compositional and microstructural characterization of Celtic silver coins from northern Italy using neutron diffraction analysis, Microchem. J. 126 (2016) 501–508.

[17] L. Fabrizi, F. Di Turo, L. Medeghini, M. Di Fazio, F. Catalli, C. De Vito, The application of nondestructive techniques for the study of corrosion patinas of ten Roman silver coins: The case of the medieval Grosso Romanino, Microchem. J. 145 (2019) 419-427.

[18] M. Di Fazio, F. Di Turo, L. Medeghini, L. Fabrizi, F. Catalli, C. De Vito, New insights on medieval Provisini silver coins by a combination of non-destructive and micro-invasive techniques, Microchem. J. 144 (2019) 309-318.

[19] A. Inberg, D. Ashkenazi, M. Cohen, N. Iddan, D. Cvikel, Corrosion products and microstructure of copper alloy coins from the Byzantine-period Ma'agan Mikhael B shipwreck, Israel, Microchem. J. 143 (2018) 400-409.

[20] Y. Nir-EI, Elemental assay of Roman silver and copper coins and associated casting items by XRF, J. Radioanal. Nucl. Chem. 219 (1997) 115-117.

[21] K. Janssens, G. Vittiglio, I. Deraedt, A. Aerts, B. Vekemans, L. Vincze, F. Wei, I. Deryck, O. Schalm, F. Adams, A. Rindby, A. Knöchel, A. Simionovici, A. Snigirev, Use of Microscopic XRF for Non-destructive Analysis in Art and Archaeometry, X-Ray Spectrom. 29 (2000) 73–91.

[22] E.L. Szonntagh, Sampling method for representative elemental analysis of non-homogeneous coins, Mikrochim. Acta 75 (1981) 191-205.

[23] P. Oliveri, M. Forina, Data Analysis and Chemometrics, in Chem. Anal. Food Tech. Appl., 25– 57 (2012), Chapter 2.

Figure and table caption list:

Figure 1. Recto and verso of 4 *folles* belonging to Class A2, B, C and J.

Figure 2. The micro-destructive sampling procedure is pictured here (a: drilling and collection of powder; b: final sampled *follis*).

Figure 3. Total mass (g) of copper in each class of coins calculated from the measured weight of *folles* and the percentage of copper.

Figure 4. Biplot (score and loading scatter diagram) from PCA: scores are depicted in bold capital letters, colored according to a chromatic scale from blue (most ancient samples) to red (most recent samples); loadings are indicated in grey italic font.

Table 1. Historical-based grouping of the 33 examined *folles*. 11 groups are identified (from A1 to J). Diameter, thickness and weight are reported for each group of *folles* (as average value and, in brackets, the standard deviation, n = 3).

Table 2. Average concentrations in percentage (wt%) for surface and bulk samples calculated using the 3 *folles* available for each class (average values are reported, standard deviation is in small font, n=3). The last row represents the average values for each metal in bulk and surface samples.

Table 3. Correlation matrix for the bulk data set (bivariate analysis). Values greater than 0.5 or lower than -0.5 are in bold.