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(Article begins on next page)

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Summary:

X-Rays are a non-destructive, element specific probe of great potential for cultural heritage. Furthermore, synchrotron radiation sources provide high intensity leading to extraordinary sensitivity. These capabilities were exploited for studying four ancient gold coins dating back to the IV and V century A.D.. Combining the complementary information obtained by X-Ray Fluorescence and Photoemission Spectroscopy, we determined the chemical composition of the coins and we assess the speciation of the chemical contaminants providing information about historical situation of the minting period of the specimens and the metallurgic knowledge available at the time.

In most cases, routine analytical methods used for the analysis of metallic samples cannot be adopted in the study of ancient numismatic objects due to their inherent destructiveness. One of the analytical techniques that allows rapid, sensitive, and accurate non-destructive microanalysis is the Synchrotron Radiation X-Ray Fluorescence (SR-XRF)(1).

In 313 A.D., Constantine I introduced a new currency: the *solidus*. It maintained high purity (gold content >90%), stability of weight and title, and high purchasing power throughout the period of its circulation(2). In this work, we analysed four gold coins (3 *solidi* and 1 *tremisse*), minted from the IV to the V century A.D., combining laboratory techniques with SR techniques available at the Elettra Synchrotron in Trieste, Italy.

Portable XRF instrument allowed to carry out an initial exploratory analysis, in which the main elements were identified. Thanks to a high purity gold standard, it was also possible to calculate semi-quantitatively the gold content of the four specimens, that was found in the range of 95-99%. However, due to the severe limitation of laboratory instruments in sensitivity, it is difficult to identify minor elements with this instrumentation. This issue was overcome using Synchrotron Radiation techniques, namely SR-XRF(3) and SR-Scanning PhotoElectron Microscopy (SPEM) (4).

SR-XRF has a detection limit in the ppm range, allowing the reliable identification of elements with an abundance of <1.0%. This is crucial for obtaining information on the origin of the primary metal, on the processes of alloy alteration and on gold purification methods. SR-SPEM, on the other hand, is highly surface sensitive, providing valuable information on the place of burial and on the processes that occurred over the centuries.

From a fine quantification analysis of SR-XRF spectra, it was possible to distinguish the elements present in the metal alloy from the contaminants. The first group includes Ag, Pb, Pt, Pd, Ag and Hg, while the second group includes mainly Al, Si, Ca, Fe and Cu.

The gold content was found to decrease with the increase of the age of mintage: at the same time, there was a higher percentage of Ag and Hg. The Pt/Pd ratio is also very informative: these two elements are commonly used as tracers of gold provenance and manufacture. A constant ratio would indicate that all the four coins share the same origin(5).
Furthermore, on the basis of the XRF maps, different areas were selected for X-ray Absorption Spectroscopy (XAS) at the K-edges of Zn, Fe, and Cu, probing the oxidation states of these elements. Combining different SR techniques with laboratory instruments, we could assess the Au purity, as well as the chemical composition of the contaminants being the fingerprints of the geographical location of the gold mine, and yielding information on the gold purification processes, on the coining materials, and on the compounds deposited during burial periods.

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