

micro-LIBS vs. XRF analysis of surface-enriched silver coins. Is a micro-destructive approach really unavoidable?

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ABSTRACT: We have performed a comparative study of micro-LIBS and X-Ray Fluorescence Spectroscopy (XRF) analysis for quantifying the silver contents in Swabian deniers minted during the Kingdom of Sicily (1194-1266). The combined use of the two techniques allowed us to validate the chemical composition of the coins and to evaluate the altered surface and the surface-enrichment treatment eventually undergone. The use of LIBS coupled with microscope allowed to reduce the dimension of the laser-induced crater below 20µm so the visual aspect of the coin remains unchanged. The LIBS measures overcome the question of the surface alteration, but they do not represent the heterogeneity of the alloy because of the small sampling area. On the other hand, the XRF technique allows to analyze a larger surface, in a totally non destructive way; however, the sampling volume could be affected by alterations or excessive roughness. It has been verified that these two factors do not affect the reliability of the measures but could introduce an uncertainty in the quantity data. The LIBS quantitative data have been obtained using the One Point Calibration method (OPC) while the XRF quantitative data were obtained by means of the Fundamental Parameter method. A good agreement between the two results was found, demonstrating the effectiveness of both the micro-LIBS and XRF techniques, in spite of the above mentioned limitations. The comparative study has been conducted on a group of 50 deniers belonging to the reign of Henry VI and Frederick II; the results confirmed the knowledge about the devaluations of the coins within 50 years of the Swabian Kingdom. A classification method has been proposed to set historically the coins.
