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The mystery of mercury-layers on ancient coins — A multianalytical study on the Sasanian coins under the Reign of Khusro II☆

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ABSTRACT

40 Sasanian silver coins of the emperor Khusro II (591–628) belonging to the Coin Collection of the Kunsthistorisches Museum Vienna (KHM) as well as 188 coins of the same emperor acquired at the free coin market were analyzed using micro-X-ray fluorescence analysis (μ-XRF) in the course of the research project "Sylloge Nummorum Sasanidarum". These studies revealed the presence of mercury in the XRF spectra of a bigger part of the coins. First investigations with complementary techniques showed that the mercury is present as a surface layer. Therefore, further detailed studies were performed on polished sections using the Particle Induced X-ray Emission technique with a proton microprobe (μ-PIXE) that offers quantitative and spatially resolved elemental information with micron resolution, scanning micro-X-ray fluorescence (μ-XRF) analyses for a better understanding of the elemental distribution on the surface and polished sections of the coins and finally confocal micro-XRF (3D μ-XRF or CMXRF) analyses for revealing information on the surface layering and elemental in-depth distribution. The synergistic application of these methods offered detailed and improved information on the structure of the mercury-layer on the surface of the silver coins supporting assumptions dating back to 1976/78 indicating medical treatments using Hg as basis for this phenomenon.

1. Introduction

The Sasanian Empire was founded in 224 AD and was one of the most flourishing and powerful states in the ancient world. It lasted until the middle of the 7th century AD. Due to the lack of other evidence, its coinage is the most important source for the study of political and economic history of the Sasanian Empire. Despite this fact, Sasanian coinage has not been studied in detail before the project "Sylloge Nummorum Sasanidarum". Currently, two of the coin catalogue series are already published [1,2] in the course of this project, each including additional scientific investigations using XRF analysis to complete the catalogue with its various studies of typology, mints, and denominations. At the moment, Volume 5 is in preparation, covering the reign of Khusro II (591–628), including also detailed descriptions, of the analyzed coins. Coins from this period are of special interest because under this king, all coins bear already mint indications and dates.

To complete also this volume, scientific investigations using XRF analysis were performed. Forty silver coins from the mints WYHC (Vēh-āz-Antiok-Kosrow, 27 coins) and AW (Hormozd-Ardašīr, 13 coins) kept in the Coin Collection of the Kunsthistorisches Museum Vienna (KHM) were selected for these studies. The analyses on theses coins have to be performed in a non-destructive manner on the obverse and reverse, although the well documented problems arising with this restriction regarding the presence of corrosion effects and surface treatments are well known [3–6]. These pose a serious limit to achieve a reliable quantification of their bulk composition. To deal with these problems 188 coins were bought at the free market. These coins can be assigned to 31 different mints, including again 15 coins of the mint AW and 20 coins of the mint WYHC, as well as 8 coins that could not be assigned to any mint because of their bad condition. All 188 purchased coins were not included in the inventory of the museum at the time of analysis and could, therefore, be cut. One small part of each of the coins was then embedded in

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synthetic resin and polished to obtain a cross-section. The residues of the coins were included in the museum inventory after the investigations and are characterized by the use of 5-digit inventory numbers. These inventory numbers are used within this paper to describe the coins.

The embedded cross-sections of the coins were utilized for micro-X-ray fluorescence (μ-XRF) and Particle Induced X-ray Emission analyses using a proton microprobe (μ-PIXE), whereas scanning 2D and 3D micro-XRF (CMXRF) measurements were carried out on the non-embedded parts of the coins.

2. Experimental

2.1. The PART I micro-XRF spectrometer

The portable focused-beam (micro-) XRF spectrometer of the IAEA (International Atomic Energy Agency), Nuclear Science and Instrumentation Laboratory, was designed to detect chemical elements from Na upwards [7]. The system is equipped with a compact vacuum chamber that can be pumped down to 0.1 mbar, minimizing absorption losses in the excitation and X-ray fluorescence radiation paths. It houses the X-ray beam optics and the detector snout. A Kapton™ window seals the chamber and allows locating the investigated spot in front of the chamber. Positioning is done by the use of two laser pointers crossing at the focal spot of the polycapillary at about 1–2 mm distance in front of the instrument and by the use of an internal camera. For focusing or collimating the primary beam alternatively either the polycapillary lens with a spot size of about 160 μm, or a collimator with a 1 mm inner diameter can be used; these are also mounted inside the vacuum chamber. The chamber is attached to a low power Pd-anode tube operating up to 50 kV and 1 mA with a point focus of 400 μm as excitation source. The fluorescence radiation is collected by a Si drift detector with an active area of 10 mm^2.

2.2. Scanning 2D and 3D micro-XRF analyses

Scanning 2D and 3D micro-XRF analyses were carried out at the home-build modular and multipurpose micro-XRF spectrometer of the Nuclear Science and Instrumentation laboratory (NSIL) of the International Atomic Energy Agency (IAEA) Laboratories [8]. It comprises of the following main components: high power (1–3 kW), line focus, Mo-anode, diffraction X-ray tube; three silicon drift type X-ray detectors (SDD) serving different purposes, namely: (1) detection of X-ray fluorescence (XRF) radiation in a "standard" geometry, (2) detection of XRF radiation in confocal geometry, and (3) detection of the primary beam transmitted through transparent samples; X-ray polycapillary lens focusing the primary beam emerging from the X-ray tube; polycapillary half-lens positioned in front of the SDD detector sitting at the right angle versus the primary beam in a confocal arrangement; a second polycapillary half-lens attached to the SDD detector positioned behind the sample working as a fine-collimator of the primary beam transmitted through the transparent samples; computer controlled, motorized sample stage with three translation and one rotation axes with additional manual tilt adjustment (2-axes) and manual xy adjustment of the sample rotation axis; the confocal half-lens motorized positioning stage with the ability to perform precise adjustment of the confocal geometry in 3-spatial dimensions (3D); a laser triangulation position sensor; an optical microscope coupled to a CMOS camera providing real-time image of the analyzed region of the sample. All components were mounted on an optical breadboard table with a passive pneumatic isolation. The scanning and the data acquisition is controlled by the SPECTOR/LOCATOR software developed in the IAEA Laboratories in collaboration with the Laboratory for Ion Beam Interactions, Ruđer Bošković Institute, Zagreb, Croatia [9,10].

The confocal micro-XRF measurements (CMXRF, see Fig. 1) [8] allow verifying the depth distribution of the elements with the only constraint arising from the difference in sample attenuation for different characteristic emission energies. The focus size of both lenses (the one used for excitation and the one used in the confocal detection channel) is of about 27 μm (Cu-K_α).

2.3. PIXE using a proton microprobe (μ-PIXE)

The μ-PIXE measurements were performed at nuclear microprobe facility of the Ruder Bošković Institute, Zagreb, Croatia. Cross-sections were exposed to the scanned 3 MeV proton beam focused to approximately 1 μm in diameter inside of the ion microprobe vacuum chamber. An electronically cooled SDD detector was used to collect the X-ray spectra. Two dimensional (2D) distributions of designated elements in cross-sections were obtained with the homemade SPECTOR data acquisition and analysis software. Quantitative analysis of the PIXE spectra was performed using the GUPIX software [11]. The sum of the concentration values of elements was normalized to 100%.

2.4. Graphical visualization

For creating the elemental distribution maps and line scan graphs the software SPECTOR [9,10] was used for both CMXRF [8] and μ-PIXE [12], which allows calculating characteristic emission peak net counts as either total counts in a region of interest (ROI) or as area of fitted Gaussian. The 3D representation of the results from CMXRF analysis was made using Avizo7 supplied by FEI [13].

3. Results

3.1. Analysis using the PART I micro-XRF spectrometer

The analysis using the PART I instrument can be divided in two sessions. In the first session the museum coins were analyzed non-destructively using the pinhole for excitation and in the second session the 188 cross-sections of the coins obtained at the free market were analyzed by employing the polycapillary lens in the excitation channel. This mode of analysis was required since the thicknesses of the coins' cross-sections were often less than 500 μm.

In both sessions five measurements on each coin/cross-section were performed using the measuring conditions indicated in Table 1. For the evaluation of the spectra the programs PMCA with XRS-FP of Amptek, Bedford, USA and the WinQXAS of the IAEA were used.

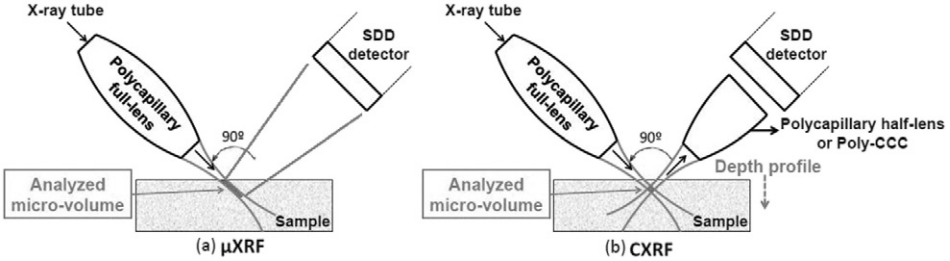

Fig. 1. Comparison of the inspected volume for μ-XRF (a) and CMXRF (b).