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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.

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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 these 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 ($\text{Cu-K}\alpha$).

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

The μ -PIXE measurements were performed at nuclear microprobe facility of the Ruđer 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.

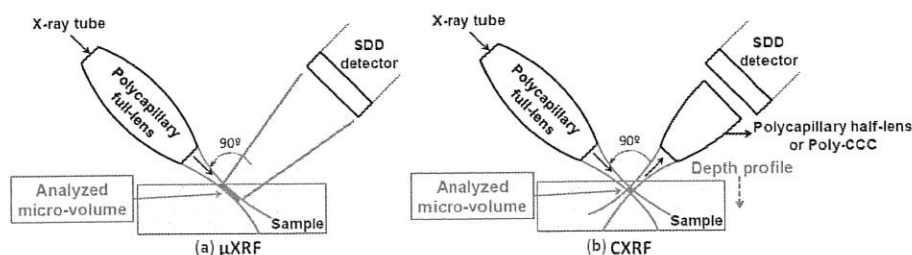


Fig. 1. Comparison of the inspected volume for μ -XRF (a) and CMXRF (b).

Table 1
Excitation conditions for the measurements with the PART I instrument.

Excitation conditions	
Voltage	50 kV
Current	1 mA
Vacuum	Yes
Filter	No
Livetime	200 s
Collimator	Used for museum coins
Polycapillary	Used for cross-sections

The analysis of the forty museum coins from the mints AW (Hormozd-Ardašīr) and WYHC (Vēh-āz-Antiok-Kosrow) revealed no surprising results, except for the coins with the inv. nos. OR 6759 (mint WYHC), OR 6821 (mint WYHC) and OR 6943 (mint AW), where mercury could be detected. The quantitative evaluation yielded concentrations between 0.3–16.4 wt.% for Hg (see Table 2). It should be noted, however, that the reported Hg wt.% concentration denotes an apparent abundance of this element as if it was homogeneously distributed in the core of the silver alloy. However, due to its superficial presence, the respective quantitative data reflect actually its areal density. Moreover, when this Hg apparent concentration is approximately >1%, the reported compositional results for the rest of the alloy elements should be interpreted only on a semi-quantitative basis. In these cases, the increased localized presence of Hg would decrease the intensities of the characteristic X-rays which are emanated from the alloy core elements and consequently lower concentrations will be accordingly determined from the quantification procedure.

From the analysis of the purchased coins' cross-sections, it was evident that mercury could be detected in a large number of these coins (152 out of 188). Sometimes, again, even very high intensity peaks of Hg could be observed, for instance on the cross-section of coin inv. no. GR 42780 from the mint Ardaschir-kwarra (ART, see Fig. 2). Performing quantitative analysis on the spectra of this coin led to apparent Hg concentrations up to approximately 13% (see Table 2). These high concentrations cannot be explained with any known production process of the silver alloy. Therefore, some preliminary investigations using SEM/EDX (Scanning Electron Microscopy with Energy Dispersive X-ray spectroscopy) were carried out, leading to the conclusion, that the mercury is almost exclusively present on the surface of the coins. As applying an electron beam using SEM/EDS might lead to a depletion of the mercury [14] and the IAEA laboratories hold a couple of high sophisticated

Table 2
Semi-quantitative evaluation of the non-destructive analyses on the surfaces of the coins inv. nos. OR 6759, OR 6821 and OR 6943 and on the cross-section of the coin inv. no. GR 42780. In this later case, in addition with the other detected elements, Fe and Zn were also detected with an average concentration of about 0.47 and 0.28 wt.%, respectively.

Inv. no.	#	Ag	Cu	Hg	Au	Pb	
OR 6759	Surface	1	93.3	3.0	0.11	1.33	1.77
		2	94.1	2.6	0.09	1.22	1.51
		3	94.4	2.4	0.14	1.09	1.42
		4	94.2	2.6	0.20	1.08	1.48
		5	86.4	2.1	8.54	1.10	1.52
OR 6821	Surface	1	95.2	2.3	0.23	1.13	0.61
		2	94.7	2.5	0.29	1.28	0.66
		3	93.2	4.0	0.24	1.07	0.99
		4	94.8	2.7	0.24	1.23	0.51
		5	94.1	3.2	0.23	1.23	0.79
OR 6943	Surface	1	80.5	0.6	16.41	1.35	0.71
		2	84.9	1.3	10.97	1.32	1.05
		3	77.2	1.5	8.99	0.87	11.01
		4	87.8	1.0	7.64	1.44	1.63
		5	87.8	1.0	7.64	1.44	1.63
GR 42780	Cross-section	1	77.4	7.1	12.7	1.4	0.64
		2	81.0	9.5	6.6	1.6	0.66
		3	81.9	11.4	3.5	1.6	0.83
		4	80.6	10.1	5.9	1.8	0.90
		5	80.8	7.6	7.8	1.8	1.03

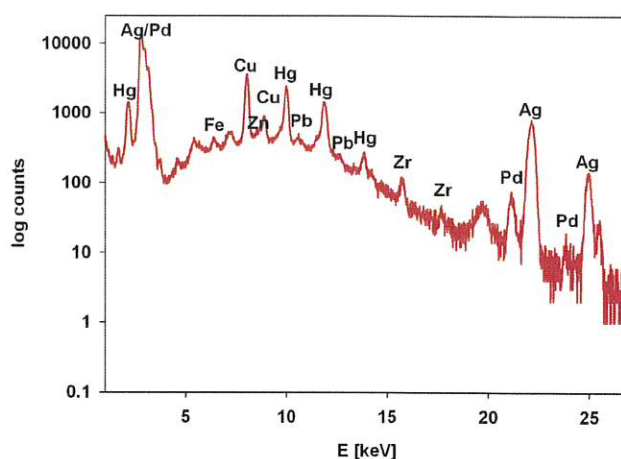


Fig. 2. Spectrum of measurement 1 on coin inv. no. GR 42780, showing mercury peaks. (The presence of Zr can be attributed to the internal Zr collimator commonly used on the chip of Silicon Drift Detectors to restrict detecting X-rays at the crystal edges).

analytical instruments and accordingly have access to facilities with additional instrumentation it was decided to perform further investigations using μ -PIXE, μ -XRF mapping and CMXRF, taking advantage of the excellent resolution, mapping techniques and 3-dimensional possibilities.

The presence of Hg in the analysis of coin inv. no. GR 42780 (as well as on the other cross-sections of the coins) can be explained by the fact that generally the cross-sections are very thin (normally below 500 μ m). The proper positioning of the coin's cross-section at the intersection of the exciting beam path (with a footprint of 160 μ m) and of the detector axis is performed by the use of two laser pointers coinciding at the measuring point. However, as the surface of the cross-sections is polished, reflections hamper the precision of the alignment procedure and surface regions could also be irradiated. As a consequence, both, the surface and core alloy elements could contribute to the measured X-ray intensities with an unknown relative contribution. For this reason, the quantitative results obtained for the coin inv. no. GR 42780 should also be treated on a semi-quantitative basis.

This means, that although the resolution of the PART I instrument is presumed to be sufficient for the analysis of cross-sections of coins, in reality the inaccuracies in positioning can lead to problems. Nevertheless, in this case, semi-quantitative analysis could be performed on all the cross-sections using the PART I instrument. Results will be published in Volume 5 of the "Sylloge Nummorum Sasanidarum".

Summarizing the investigations using the PART I instrument it is evident that on most coins acquired at the free market Hg could be detected, whereas this is only exceptional for the museum coins. It has to be stated, that for all coins the treatment regarding their surface cleaning is not known; also for the museum coins no records exist. For the coins from the free market the presence of the mercury is not in correlation with single salesmen or providers.

3.2. Particle Induced X-ray Emission with a proton microprobe

Three coins from the mint AHM (Hamadān) were investigated; on two coins Hg was detected using the PART I micro-XRF spectrometer (inv. nos. GR 42762 and GR 42777), whereas on the other one (inv. no. GR 43478) no Hg was detected with PART I.

On coin inv. no. GR 42762 the surface on both sides of the cross-section was investigated. The elemental distribution of Ag-L α , Cu-K α and Hg-L α characteristic X-rays is reported in Fig. 3 corresponding to a total scanned area of 125 \times 125 pixels or about 90 μ m \times 90 μ m. Within the core of the coin, some inhomogeneities of the silver/copper content

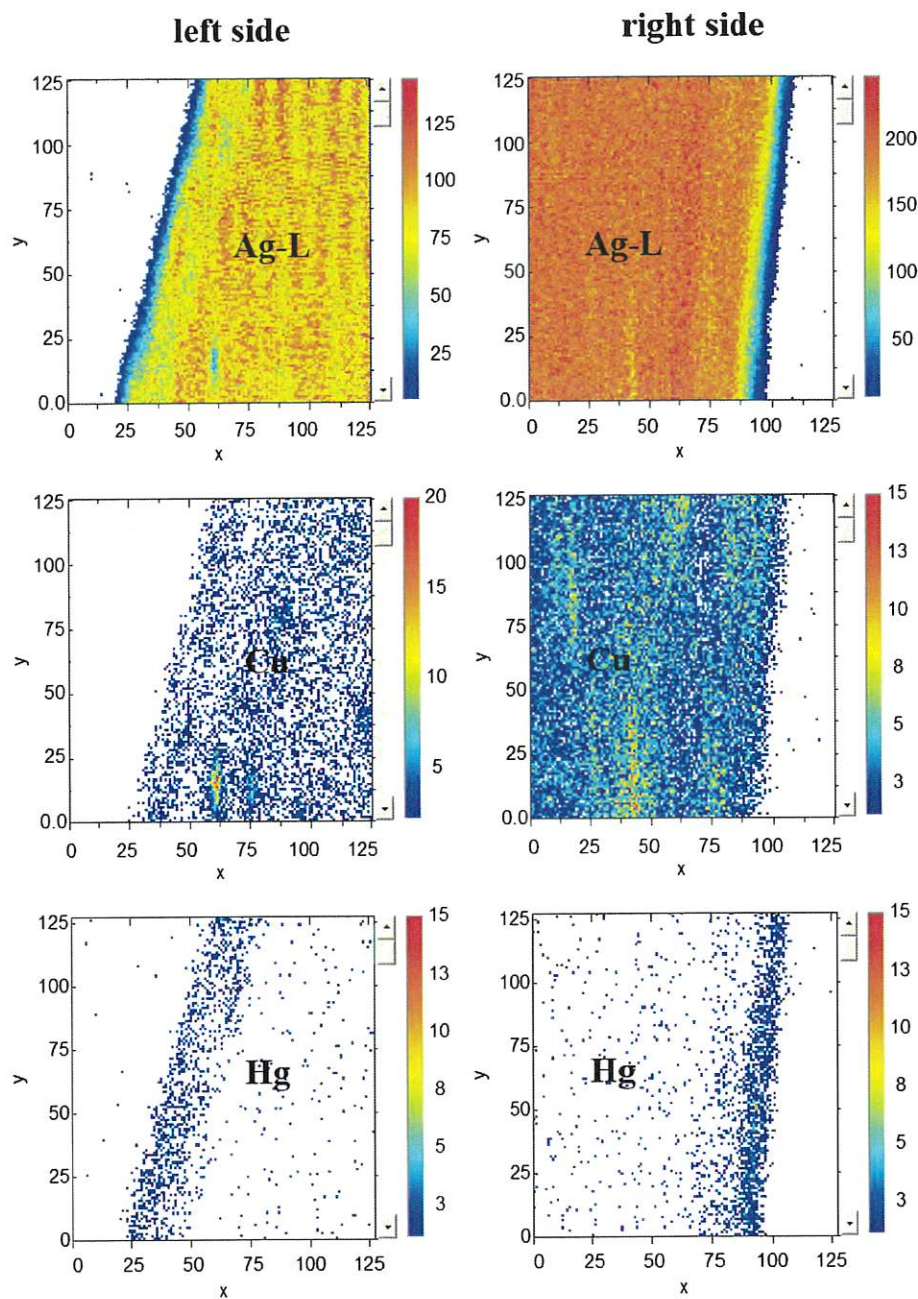


Fig. 3. Elemental distribution of Ag-L_α, Cu-K_α and Hg-L_α characteristic X-rays on the cross-section of coin inv. no. GR 42762 (x and y scales in μm).

are observed. The composition of the core alloy could be determined to be approximately 94% Ag and 4% Cu with some traces of Pb and Au.

The Hg containing surface layer is appreciable from the elemental maps. Within this superficial layer of about 10 μm a gradual depletion of silver is observable, whereas the Cu concentration remains more or less constant within the core and the surface layer. These observations are somehow confirmed when projecting the sum of characteristic X-ray intensities recorded in all y pixels (from 0 to 55 with a length of about 40 μm with reference to area maps of Fig. 3) into the horizontal x-axis (Fig. 4). This procedure was followed to overcome the limitations arising from the poor counting statistics of individual pixel measurements. The thickness of the layer is overestimated as $1 + \sin(\theta)$ (θ being the tilt angle of the surface regarding to the y-direction of the scan) but considering that the angle was less than 10° and that the

thickness of the layer is somehow constant, the obtained value can be used as an estimate.

On the first sight the presence of Ag and Cu in the Hg layer seems rather intriguing, but it could be explained by the formation of some Ag- and Cu-amalgam that is considered thermodynamically possible: Diffusion happens for all the components in the system, i.e. Cu into Hg, Ag into Hg and vice versa but smaller atoms can diffuse faster into the lattice of the larger atoms [16]. Cu is the fastest atom in the system, diffusing mainly into the lattice of the largest atom, i.e. Hg, forming an amalgam [17]. The diffusion of Hg into the Ag/Cu matrix is on the other side negligible. Nevertheless, also for copper the diffusion into the app. 10–20 μm thick Hg-layer needs some hundred years or even more, and it is easy to understand that the diffusion of Ag is dramatically slower than that of Cu, taking into account the diffusion coefficients

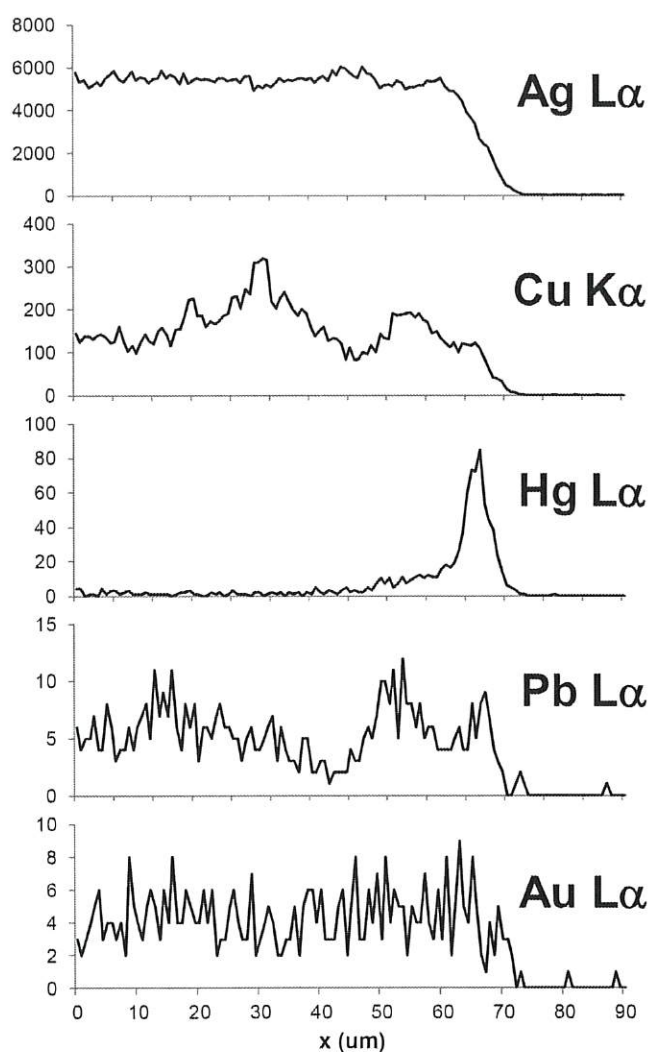


Fig. 4. In-depth distribution of Ag, Cu, Hg, Pb and Au content for the coin inv. no. GR 42762. The x-axis projected K_{α} (Cu), L_{α} (Ag, Hg, Pb, Au) net peak areas were summed from y-pixel 0 to 55 (of equivalent length of about 40 μm). The spectra analysis, due to its particular complexity, was carried out in batch mode by means of bAXIL software [15].

[18]. If shorter times (than app. 1000 years) are considered for the diffusion in the present system, the diffusion rate would be far away from the typical diffusion rates (and diffusion coefficients) for solids at nearly room temperature [19]. So there are scientifically provable facts for the assumption that the Hg layers date back to early history and do not refer to present times.

These observations could also be confirmed considering the elemental distribution of coin inv. no. GR 42777, though the mercury layer in the investigated area is not as prominent as on coin inv. no. GR 42762: On one side hardly any Hg layer is observable, whereas on the other side the Hg layer is clearly visible, again showing the inhomogeneous thickness of this surface layer.

On coin inv. no. GR 43478 no mercury layer was detected using the PART I spectrometer. This could also be confirmed by μ -PIXE. Instead, in this case a contamination with Fe was visible. As this was only a singular observation it may be connected with the burial conditions, as iron is contained only in trace amounts in the core of the silver alloy.

3.3. Micro-XRF analysis performing 2-dimensional scans

2-Dimensional scans were performed using the μ -XRF system of the IAEA, Nuclear Science and Instrumentation Laboratory. These

measurements were performed on the non-embedded parts of the purchased coins to obtain a larger overview of the elemental distribution on the cross-sections of the coins as well as on their surfaces. The measurements were performed with a step size of 25 μm (x and y displacement directions) with an excitation beam of 27 μm (for $W-L_{\alpha}$) in diameter.

The investigations were carried out on two more coins, inv. nos. GR 42820 and GR 42791, this time from the mint WYHC (Vēh-āz-Antiok-Kosrow). The mercury layers could be found on both coins but as the layering of coin inv. no. GR 42791 is the more interesting one, only the investigations on this coin are shown. The whole cross-section, app. 18 mm \times 0.5 mm, could be scanned and the results are shown in Fig. 5. Mercury and lead were found in specific spots or areas in the edges of the cross-section (averso and reverse surfaces of the coin), but not to be uniformly distributed over the whole length of the edges. Therefore, it was decided to make large 2D maps of both surfaces of the coin, trying to find the overall distribution of elements over the surface, as shown in Fig. 6. Regarding these maps, lead can be found mostly in the 'valleys' between the relief decorations (obviously in accordance with the light gray areas visible on the surface), whereas the highest values of mercury are in the edges and slopes of the relief ornaments. As this pattern is found in the valleys of coins, it seems as if the coin was contaminated with Pb – most probably it was buried together with some lead material – and cleaned/polished after it was excavated. The ornament was made visible but the contamination "survived" in the valleys.

Normal μ -XRF investigations show as disadvantage that they provide information not only from the uppermost layer but also from the effectively detected layer below the surface. Therefore, to enhance the resolution also into the depth, CMXRF measurements were performed.

3.4. Confocal micro-XRF analyses (CMXRF)

Confocal measurements were made to elucidate the distribution of mercury and lead over the surface elements, and to evaluate the thickness of their layers.

Line scans were also carried out perpendicular to selected spots at the surface of coin inv. no. GR 42791. The selected spots correspond to areas of maximum intensities of mercury or lead (obtained from the previous μ -XRF scans) and are shown in Fig. 7. The scans were performed with 1 μm steps, starting from approximately 50 μm below the surface and with a total travel path of 100 μm .

The results were similar for all the line scans and are depicted in Fig. 8. The higher resolution of the CF setup allowed establishing the sequence of the element layers, thus revealing additional information: The Pb layer can be found on top of the Hg layer that lies on top of the Ag/Cu core of the coin.

Simultaneous 2D and 3D confocal scans were made in one of the cross-section areas exhibiting higher contents of mercury and lead (spot no. 5 in Fig. 7, optical microscope image in Fig. 9). The scan was performed with 20 μm steps in x- and y-displacement direction and with 10 μm steps in z-displacement direction (depth). The inspected volume size was 1800 \times 600 \times 100 μm .

The 2-dimensional CMXRF maps shown in Fig. 10 represent the stack of the 10 z-planes (parallel to the cross-section's surface) and illustrate the improved contrast obtained by using confocal measurements as compared to conventional μ -XRF scans. Conventional μ -XRF, as resulting from the total effective depth probed (see illustration in Fig. 1) does not provide an accurate distribution of the contours in the cross-section's surface. The detection of material below the uppermost surface, as well as some effects of the coin surface topography behind the cross-section's surface, leads to a blurred representation of the elemental distribution. With CMXRF, therefore, an improved contrast can be achieved.

The performed CMXRF scans allowed corroborating the findings from the line scans, thus establishing that in this case both, mercury and lead, are present as surface layers, the Pb layer located on top of

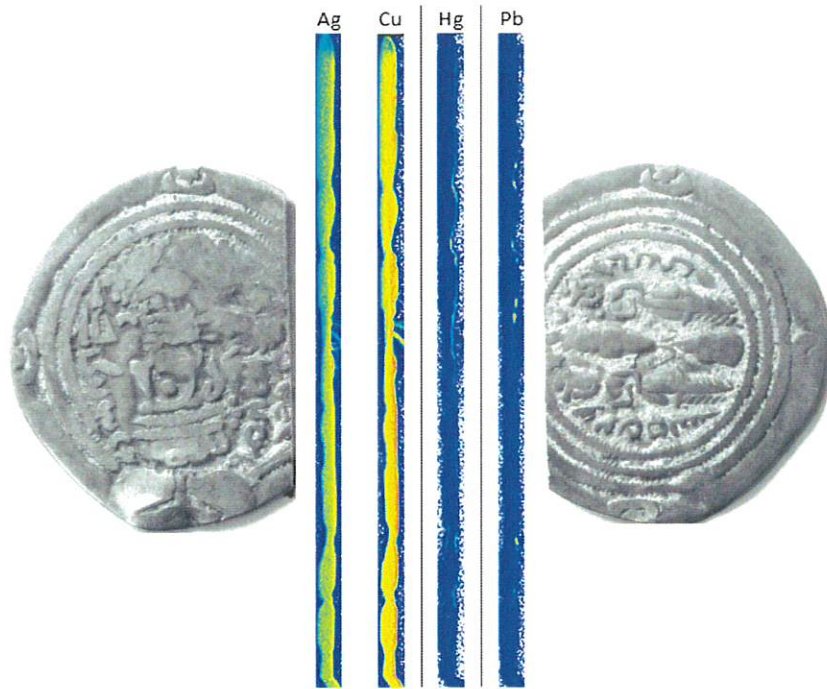


Fig. 5. Elemental distribution of the cross-section of coin inv. no. GR 42791 obtained using the μ -XRF system of the IAEA.

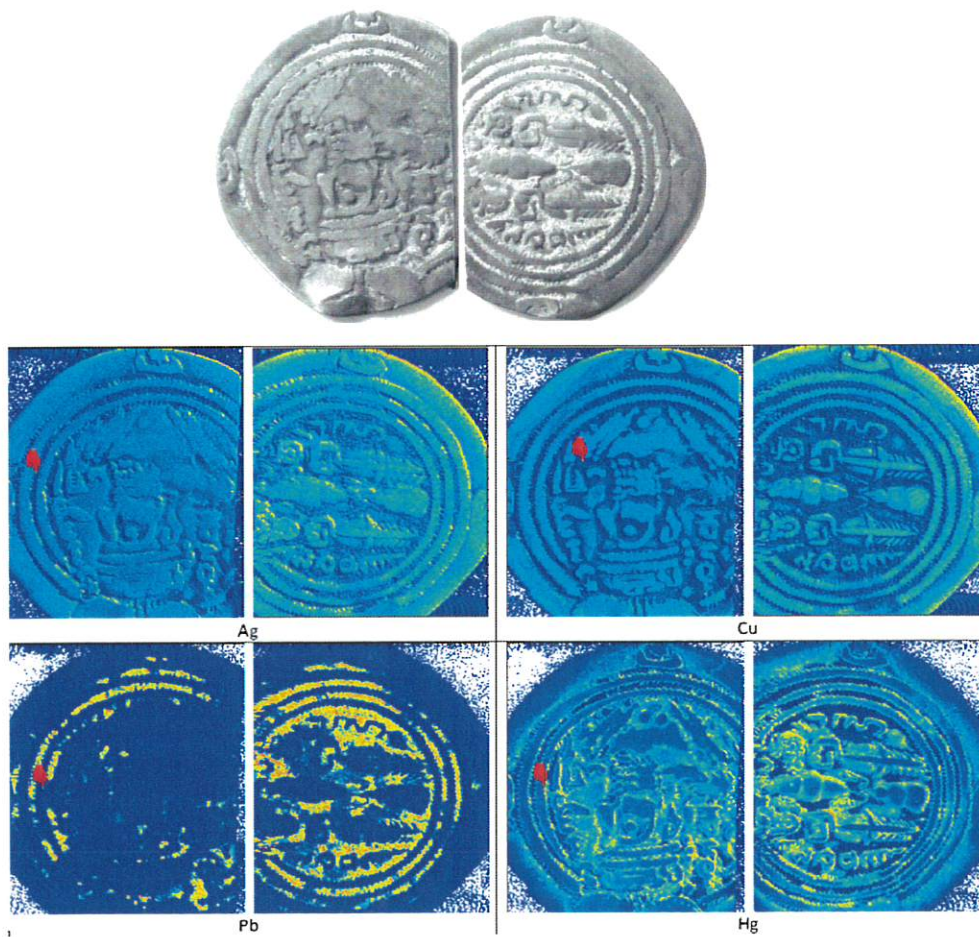


Fig. 6. Elemental distribution of the surface of coin inv. no. GR 42791 obtained using the μ -XRF system of the IAEA.

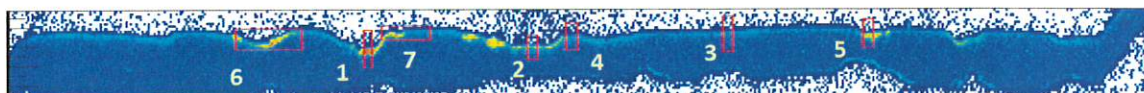


Fig. 7. Cross-section of coin inv. no. GR 42791 with indicated positions for linescans.

the Hg layer. This is a very important observation, indicating that the Hg layer is older than the Pb layer as it is the lower one. As the Pb layer could only be found on coin inv. no. GR 42791 it is very likely a contamination from burying the coin together with other items, and, therefore, the second evidence of the Hg layer being ancient.

The 3D reconstruction of the inspected volume measured by CMXRF is represented in Fig. 11. Here, again, the 2 layers are visible. The Hg layer, nevertheless, can be identified on the whole surface, whereas the Pb layer is only present partially.

To use the excellent resolution of the CMXRF technique also for the surface analysis another 3D scan was made, this time from the coin surface to greater depth. A distinctive part of the surface was selected for this purpose, shown in Fig. 12.

The scans were made with a step size of 50 μm for x and y displacement and with 10 μm for the depth. The inspected volume was 7000 \times 2500 \times 150 μm (x,y,z).

The 3D reconstruction (Fig. 13) of the surface with the confocal results shows again that the lead can be found in the valleys. The mercury can be seen re-appearing from underneath the lead layer again in the slopes. There is also some mercury visible in the higher parts of the topography, but due to the probable cleaning and/or usage of the coins the thickness of the layer drops strongly. The apparent absence of silver, copper and mercury in the “valleys” is explained as only the topmost layers are displayed.

The confocal measurements allowed revealing the surface and depth distribution of lead and mercury. The arrangement of the layers with lead on top of mercury suggests that these two elements are present on the coin surface as the result of two different processes/interactions.

4. Summary and discussion

Summarizing all results using $\mu\text{-XRF}$, 2-dimensional $\mu\text{-XRF}$, CMXRF and $\mu\text{-PIXE}$ the following observations can be made:

- The coins consist of a Ag/Cu core with a Ag-content of 77 wt.%–97 wt.%, only very few coins show a much lesser Ag content. The trace elements are Fe, Au and Pb.
- Hg can only be found on the surface of the Sasanian coins.
- The 40 coins belonging to the Coin Collection of the KHM were analyzed non-destructively from the surface. Only on three coins a Hg-layer could be detected. There are no records for their treatments in the past regarding cleaning and conservation. Nevertheless, it seems as if the Hg layer was probably removed during cleaning of the coins, indicating, that it can be removed quite easily.

- Hg could be found on 152 out of 188 coins (app. 80%) acquired at the free market. Again all treatments in the past performed from the collectors, tradesmen and excavators are not known. The presence/absence of mercury is not connected with the person from whom they were acquired, nor with single ancient workshops. On the four coins showing extremely low Ag concentrations no Hg layer was detected using $\mu\text{-XRF}$.
- The Hg containing surface layers show very heterogeneous thicknesses, within one coin as well as across different coins. Although Hg can also be detected on the upper parts of the topography, it is better preserved in the lower parts, such as valleys and slopes.
- The Hg layer does not show high concentrations of Au, therefore, fire gilding can be excluded.
- Sometimes a Pb or Fe layer can be found on top of the Hg layer. As these contaminations are most probably artifacts of burying the coins together with other objects of different material, the Hg layers need to be older than these contaminations, and are therefore probably ancient.
- The investigation of a relatively thick part of the Hg layer using $\mu\text{-PIXE}$ with a resolution of 1–2 μm beam diameter showed that there is a gradual depletion of Ag in the Hg layer, whereas the Cu concentration is more or less the same in the core material and the surface layer. This may be due to slow thermodynamical processes leading to the formation of Ag amalgam and Cu amalgam. Also this observation is an evidence for the Hg layer being ancient, because processes like these need some hundred years.

Altogether it seems as if the Hg layers are ancient. Still, the presence and the reason why they appear is a mystery. There are no ancient reports of techniques producing Hg layers known to the authors. Also silver plating is regarded as not suitable for coins with a relatively high Ag content. The fact, that the bigger part of the coins is affected leads to the assumption that it was a very common technique/effect. Furthermore, as the Hg layer seems to be removable quite easily – closer investigations to this assumption are still missing, but would be worth further examinations – it is not quite unlikely that the remaining 20% may also have been treated in the same way, but the Hg layer was lost in (probably) recent time. Regarding this fact, investigations on 30 Sasanian coins published by M. Hajivaliei et al. [20] should be mentioned. These coins are also property of a museum (Avicenna museum in Hamedan) and no Hg was detected investigating these coins non-destructively using PIXE on the obverse and reverse. In this paper the cleaning of

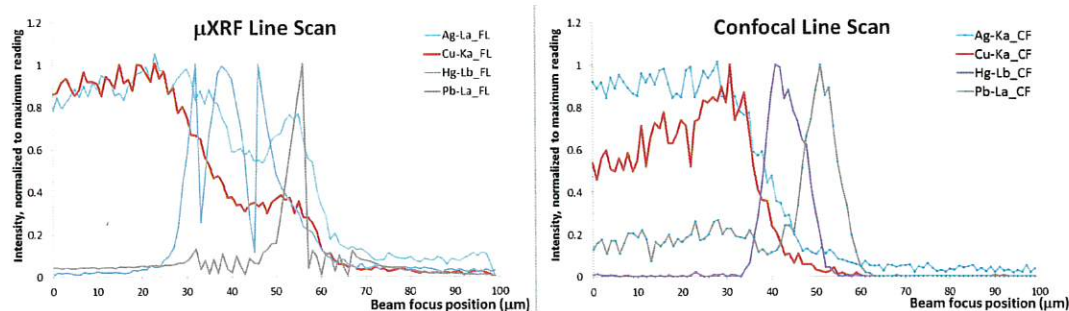


Fig. 8. ROI-intensity for the studied elements versus beam position (linescan). “0” in the x-axis represents the initial position, selected at half of the cross-section’s thickness. Left graph: μXRF scan, right graph CF scan.

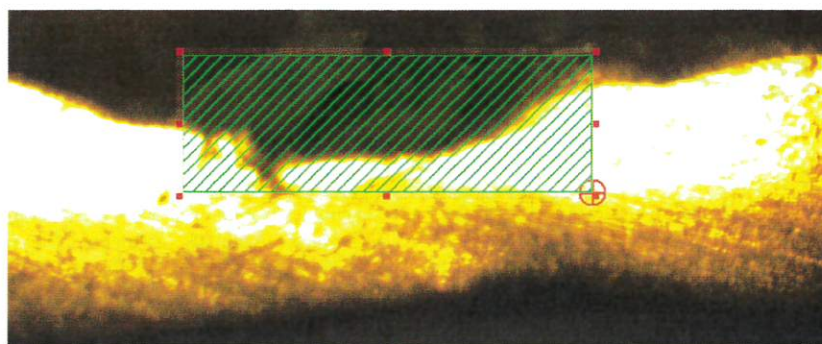


Fig. 9. Optical microscope image of the inspected area on coin inv. no. GR 42791 (spot no. 5 in Fig. 7).

the surface of the coins is mentioned; 5% formic acid solution was used for cleaning before the analysis. It is unclear if there might have been any further cleaning before. Nevertheless, this treatment as well as heat-treatment should be included in coming investigations.

Hg was also found by M.M. Al-Kofahi and K.F. Al-Tarawneh, who analyzed ancient Silver Dirhams from the Ayyubid period (1167–1248 AD) and the Mamluk period (1248–1459 AD) [21]. In most of the coins at least traces of Hg were detected. Nevertheless, the investigations were performed on the surface of the coins using XRF, but no investigation on the exact location of the Hg was done and it is not clear if a Hg layer is present, although it seems quite likely. Nevertheless, the cleaning in this case was performed by the use of water, soap and a steel brush, dried with a clean piece of cloth. The last cleaning was performed by the use of soft cotton and acetone. Also J.M. del Hoyo-Meléndez et al. [22] describes the presence of traces of Hg in medieval Polish silver coins (996–1034 AD). Surface analysis was performed using XRF. The exact position of the Hg was not examined and therefore explanations like Hg being from the extraction process of silver or from re-melting of medieval Islamic coins are given.

Also some smaller findings of Hg or Hg-layers are reported [14,23].

The first findings of Hg on ancient/medieval silver coins were published in 1975 by T. Florkowski and Z. Stós-Fertner [24]: Hg could be found on a great percentage of Arabian Silver-Dirhams (800–1000 AD). Follow-up examinations using XRF on 200 Dirhams (718–961 AD) [25] could prove this assumption [26]. One Dirham was sacrificed for the preparation of a cross-section and it was found that the Hg was only present as an approximately 10 μm thick surface layer.

Jüngst [26] picked up the question of the signification of an Hg layer on apparently high quality silver coins and turned the attention from a volitional process to a more or less accidental happening of applying a mercury layer: He cited first written experiences with Hg as a healing agent back to app. 200 AD. It was used from ancient times as ointment (Hg mixed with fat) as well as powder (Hg mixed with chalk or sulfur) and as Hg vapor to help against skin diseases and vermin like lice. The vapor treatment was often carried out with the whole garment and body in a kind of box where only the head looked out. The ointment was used e.g. to treat especially the hairy parts of the body or to rub the underwear. As money in these days was carried mostly under the shirtwaist or in a money pouch under the garment the money was exposed to mercury, either through Hg vapor treatment or treatment of

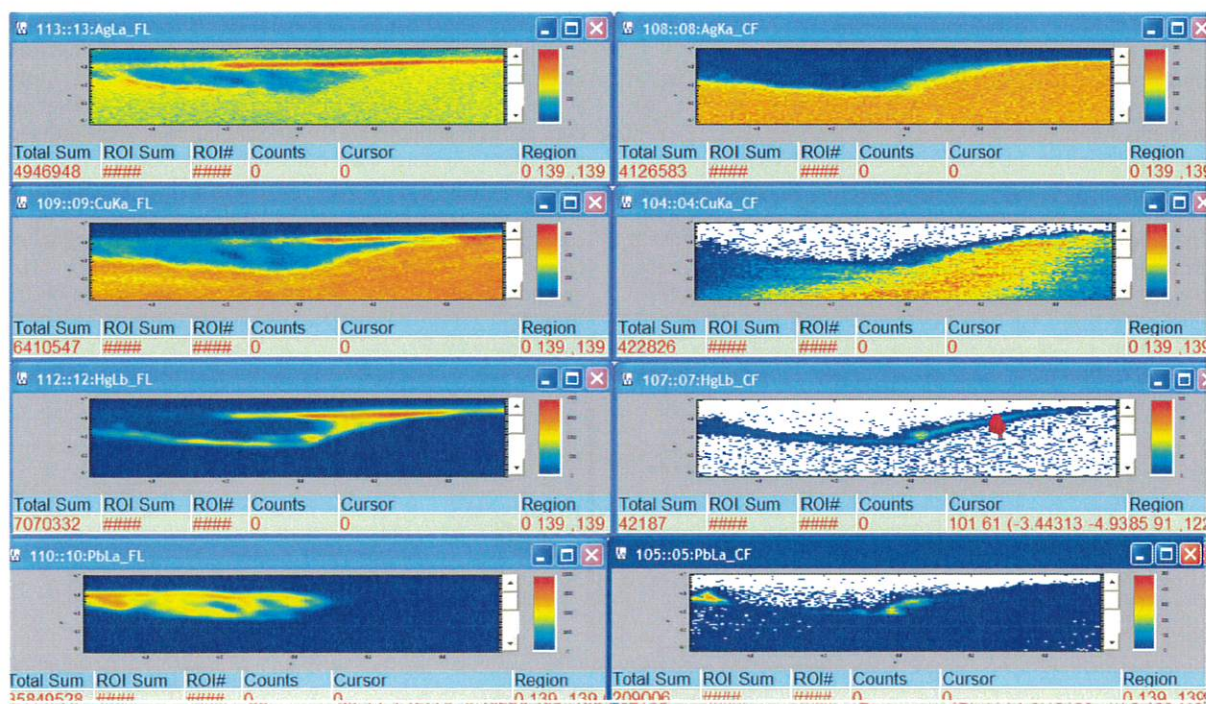


Fig. 10. Elemental distributions on the selected cross-section of coin inv. no. GR 42791; Left: μ -XRF, right: CMXRF.

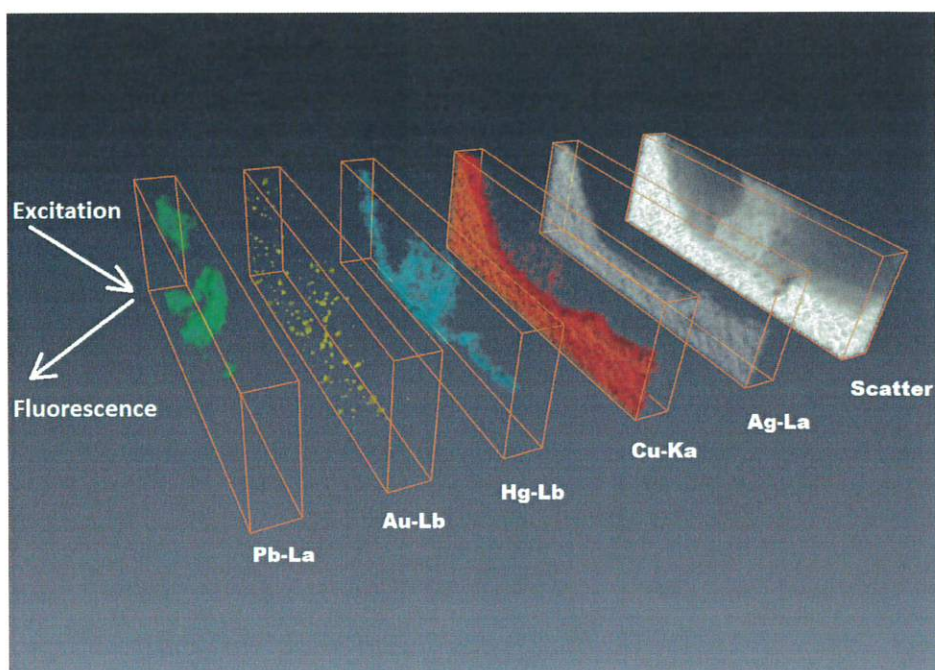


Fig. 11. 3D reconstruction of the inspected volume of coin inv. no. GR 42791 (see Fig. 9). The left plane represents the polished area of the cross-section facing the detectors.

body parts and clothes. It is obvious that especially merchants at this time had to prepare against vermin because they had to sleep in foreign accommodations during their long journeys.

Reports of Hg layers on ancient early medieval coins are only known on silver coins nowadays. This might be, because the color of a Hg layer does not attract attention on these coins as Jüngst [26] pointed out. Hg layers for example on gold coins would lead to “whitening” that could be easily removed by moderate annealing of the coin. Jüngst cited an accidental incident where this phenomenon is reported together with the successful removal of the Hg [27]. Nevertheless, closer investigations of coins made of other alloys than silver (e.g. gold, bronze) of the era of interest could provide important information to prove this assumption.



Fig. 12. Analyzed area of the surface of coin inv. no. GR 42791 using CMXRF.

Jüngst pointed out, that there is no possibility to be really sure about his theory and silver amalgamation of silver coins might be a possibility, although we nowadays do not see any sense in it. Our investigations now showed that there is a depletion of silver in the mercury layer from the core to the surface [see Figs. 3 and 4]. This is an evidence that no silver amalgamation was performed on our coins.

Also D. Sommer et al. referred to Jüngst as explanation for the occurrence of Hg layers on 10 Arabian and one Spanish Dirham (8th to 10th century AD) [28].

First considerations of the research group in Leibniz were in the same direction: It may be possible, that the coins were treated with a mercury containing cream or ointment [29–32], to make the coins shinier and/or to get rid of bad smells. Nevertheless, if this would be the case for the majority of coins showing mercury layers this must have been a more or less systematic treatment.

To find some evidence to proof the last assumption some first investigations on organic residues in the Hg layer have been performed, but the research is still in progress. Additionally, the authors are very interested in the formation of collaborations with scientists who found similar phenomena.

Nevertheless, the approach of Jüngst seems very reasonable and would also give an explanation for the different degree of contaminations of the coins and the absence of the Hg layer on a smaller fraction.

5. Conclusions

On the example of the Sasanian silver coins the different potentials, advantages and disadvantages of μ -XRF, 2-dimensional μ -XRF, CMXRF and μ -PIXE could be shown very impressively. It also turned out very useful to perform stepwise one method after the other having basic knowledge of the results of previous methods indicating the direction in which the investigation should go and the requirements to solve the existing problem. For instance, the surface analysis (Fig. 13) using CMXRF took a whole week. To perform an analysis like this it is necessary to be sure from previous investigations that it is worth the whole effort.

Additionally, the question, if the mercury layers found on the surfaces of the coins are ancient, could be solved. There are

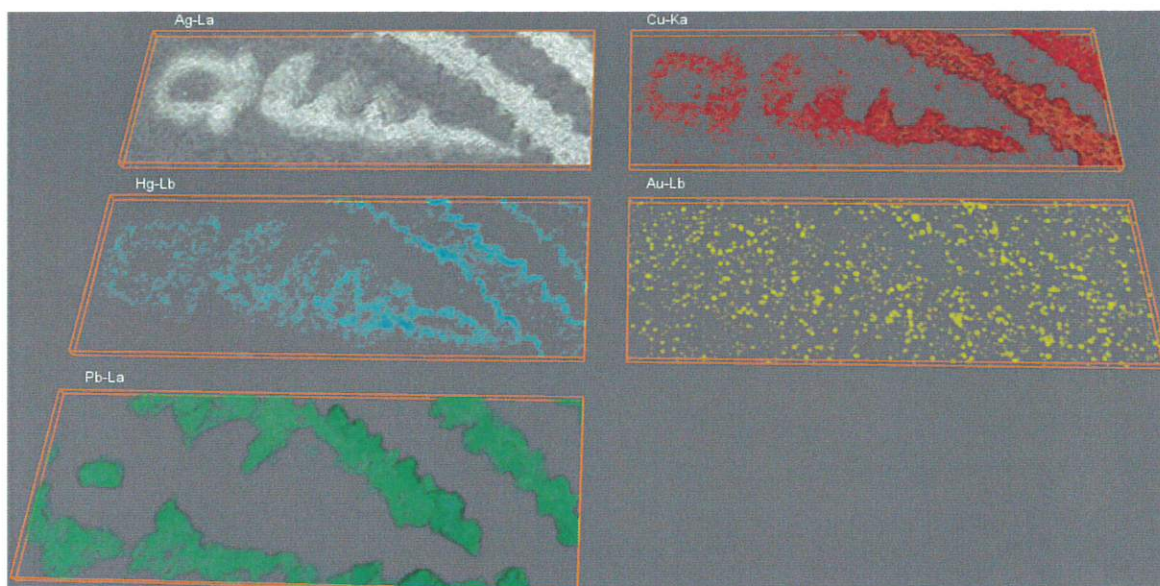


Fig. 13. 3-D reconstruction of the analyzed surface region (see Fig. 12) of coin inv. no. GR 42791 using CMXRF.

thermodynamical effects that strengthen this theory and also contaminations on top of the mercury layers lead to the assumption that the mercury layer is most probably ancient.

The purpose of this mercury layer is not completely clear. The interpretation is complicated by the fact, that only the bigger part, app. 80% of the cross-sections, is affected. For the remaining 20% the interpretation is not clear. Whereas for the fraction of the museum coins it seems very likely (although not reported) that the mercury layer was lost due to cleaning, it is completely unknown what happened to the Hg-free fraction of the coins of the free market. Hg is not an indication for a special dealer or an ancient workshop. The most convincing explanation for the occurrence of the Hg layer lies in the application of Hg for medical purposes. It may be simply a contamination from Hg, applied by vapor treatments of people or the use of Hg ointments. The latter could also be used directly to make the coins shinier or to get rid of bad smells. Nevertheless, this stays an open question and investigations are still ongoing to bring more light into this remarkable matter.

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