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POLISH RESEARCH INTO MEDIEVAL AND MODERN COIN METAL: ANALYTICAL REMARKS

Beata Miazga

Summary

1. The physical and chemical methods, which are offered by literature (Denker *et alii* 2005 65-70; Trampuž Orel and Drglin 2005 44-50), are not proper for our coin investigation. Because of a great heterogeneity of analyzed samples (seen also in macroscopic scale) the methods with visual preview and possibility of choosing an analysis area are more adequate. The place should be independent from changes on the surface connected with corrosion, exploitation, deposition and conservation processes made on historical objects.

2. The very sensitive and precise ICP-OES method is the least proper for coin analysis, because of the possibility of destruction of the coin during sampling. Comparing the results of coin no.6 analysis both by invasive technique (ICP-OES) and non-destructive, we can see the similar results in silver and copper composition. However, tin identification was impossible by ICP, probably because the sample was too small or the analyzed solution was too dilute and the Sn concentration was to low (below the determination level).

3. All these remarks focus on coins with clean surfaces, that come from a museum or other collections. However, coins from archaeological excavations are another group of artifacts. The proper cleaning of surface and the effects of previous conservation work are the big challenges. Such information is extremely important when the analyst doesn't have the basic principles of conservation or restoration and doesn't take in during analytical procedures. Cleaning and disposing of corrosion and impurities often change both a surface and a core (damage coins). One of such effects is silver surface enrichment (Beck *et alii*, 2004 153-162). Other results are connected with chemicals, which are used during conservation processes. Those substances could radically change the chemical composition. Improper chemicals (e.g. strong mineral acids of Coca-Cola) dissolve not only impurities (soil or corrosion products), but can leach non-noble metals (side elements presented in coin alloy). Hot minerals acid could damage bronze coins, because they are able to leach even copper from a surface. The caustic soda (NaOH) solution is dangerous for lead artifacts (because of extraction of lead traces from coin alloys or complete dissolution of artifacts (e.g. weights). Conservation tools represent another problem. Mechanical cleaning is an important step, after which the state of preservation is determined and the proper procedures are chosen. During this step artifacts could be sometimes damaged or contaminated. The consequences of poor knowledge of material science (e.g. hardness) could be catastrophic for coin and for the analysis. In practice many negative effects have been met, e.g. scratches after mechanical cleaning, gilding the silver coin surface by brass brushes application or enrichment artifacts by nickel and iron by steel tools. For this reasons in correct analytical investigations of artifacts (including coins) at least three researcher should cooperate: the excavator (archeologist, numismatist, art historian) and the conservator and analyst (physicist, chemist). This cooperation leads to a better understanding of problems, allows to ask proper questions and could guarantee the success of the investigation.

In 2007 a large research project has been started in the Institute of Archeology (University of Wrocław, Poland). One of the aims of this project was the preliminary physical and chemical coins investigations, which were made with different analytical methods. The basic analysis were carried out on low-historic value group of coins, which could be destroyed during experiments. Our investigations focused on the establishment of the best procedures, which could be applied to the analysis of the special and unique artifacts. For this reasons many different tests of various steps of analytical process were made:

i) the photographic documentation and the measures of fundamental properties (e.g. diameter, weight)

ii) the sample preparation (cleaning the surface of artifacts in order to remove impurities (soil and corrosion layers – coins from archaeological excavations; dust and conservation coatings – coins from museum and other collections)

iii) the choice of representative area of a sample and preparation for analysis

iv) the analytical measurements.

Most stages of investigations were made in the Laboratory of Archaeometry and Conservation of Artifacts (Institute of Archaeology, University of Wrocław), but some of them in different laboratories in Wrocław:

i) SEM-EDX (scanning electron microscope with energy-dispersive) in W. Trzebiatowski Institute of Low Temperature and Structure Research, Polish Academy of Sciences

ii) ICP-OES (induced coupled plasma-optical emission spectroscopy) in the Laboratory of Cultural Heritage Investigation, Faculty of Chemistry, University of Wrocław

iii) ED-XRF (energy dispersive X-ray fluorescence) in the District Assay Office .

The main step was an appropriate sample preparation, which included cleaning the coin sample from different impurities. The contamination layers were disposed according to the conservation and restoration methods and procedures, as one of the authors is a specialist in conservation work as well as and archaeomtery. At the beginning samples were cleaned mechanically, with prosthetic and dentist's tools (polymer brushes, which avoid making scratches on soft metal surfaces, especially silver and gold). After mechanical cleaning from dusts, the organic residues (*e.g.* fats) were extracted in the ultrasonic tank. In the bath the mixture consisted of distillation water and chemicals for jewelry cleaning (Ultra-Clean, Heimerle+Meule). The following parameters of ultrasonic cleaning were used: 4% solution of Ultra-Clean, distillation water, 120 sec. Afterwards, the coin was boiled in distillation water and dried in alcohol bath (soaking twice in a pure ethanol) and in a laboratory dryer (80°C). Coins, ready for sampling, were packed into small polymeric bags (PE). The ultrasonic cleaning is a very fast and effective cleaning method of coin surfaces, as the result of such cleaning the nominal "Einen thaler" appeared on the surface of coin number 2 - see Fig. 1.

Figure 1 — The effect of ultrasonic cleaning of coin number 2.

The second step was connected with choosing the representative area of a sample and preparing it for analytical measurements. For each method different preparation procedures were used:

i) ED-XRF and SEM-EDX. The coin samples were polished with special devices (Struers, LaboPol 5) in order to prepare a coin sample for the interaction with X-rays (XRF) and electron beam (SEM). Because these methods can be applied only for surface analysis, the samples have to be prepared in an appropriate way. The edge of coin was grounded and polished with abrasive materials of different grain size. Craters after drilling (for ICP-OES) are used for microscopic and quantitative analysis.

ii) ICP-OES – The cleaned coins have to be sampled before spectroscopic measurements. For sampling, an electronic table drill, Flott 4, with a very thin drill, was chosen (changing the spindle on smaller one using Dremel accessories, *the 400 Series*). In the samples many holes were drilled, changing drill size using a range 0.2, 0.5, 0.7 and 1.00 mm (Fig.2). For testing cobalt-steel drills were used (type HSSe/Co).

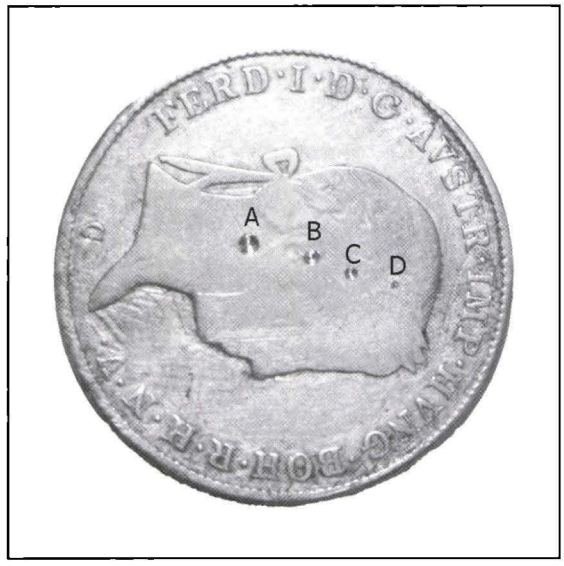

Figure 2 — The picture of the coin number 6 after using drills with diameter 1.0mm (A), 0.75 mm (B), 0.5 mm (C) i 0.2 mm (D).

Considering use of different drills (in range 0.2-1.00mm) for making holes we had to reject drills thicker than 0.2 mm, because of the possibility of coin destruction and a big change not only in a macroscopic view, but also in the mass (the average mass is more than ten milligrams).

The aim of further investigations concerning the representative area is drilling holes in various parts of artifacts, especially a coin. It was expected that the centre of coin could be the best place for drilling, but this place is often too visible and it would limit the possibility of coin exposition. Therefore it was decided that holes should be made in less visible places, situated on the radius of a coin, distant from the centre (Fig. 3).

Figure 3 — The picture of coin number 2 with the analyzed point, localized on radius of the coin.

The obtained results are presented in table 1.

Table 1 — The chemical composition of coin number 2 as a function of localization on the radius.

Chemical composition, % (w/w)	the centre of a coin ⟶					the external edge
Cu	51.14	54,42	51,19	50,24	52.11	54.72	52.21
Ag	48.67	45.37	48.58	49.58	47.71	44.88	47.33
Au	0.00369	0.0122	0.00376	0.01041	0.01781	0.01378	0.01695

Considering the experimental issues presented in table 1, we can conclude that there is a good correlation in quantitative results and the edge of a coin is a very interesting sample point for investigation. The presence of differences resulted from chemical inhomogeneity of the alloys. However, the edge of a coin should be scrupulously prepared. There are a few ways of coin preparation for non-destructive analysis, including core and surface preparation. The analysis of the core, interior bulk of the coin is restricted because of a limited access to different research methods (theoretical and practical) (Milazzo 2004 683; Beck *et alii* 2004 153). Milazzo shows on one figure in his paper the cross-section of a coin and possibilities or restriction of analysis. According to him it could be decided that core analysis is possible only by NAA (neutron activation analysis) or after core exposure (making holes or polishing the edge).

In the following investigations on the representative area, we had to analyze and consider big non-heterogeneity of the coins. Often we had to make more singular measurements, because according to statistic requirement we had to have minimum 5 or 6 similar results. For archaeological samples with significant inhomogeneity, sometimes more than 10 measurements have been made. Because of heterogeneity of an alloy and necessity of appropriate sample preparation, special tools and equipment should be applied for sampling and sample preparation. After quoted articles (Weber *et alii* 2000 724; Nir-El 1997 115), small drills were investigated. The results were not satisfactory. First, the crater, which was made, has a cone-shaped bottom, unaccepted in two beams of X-ray analysis. Those beams should be focused on a flat area. The other tool — a cylindrical cutter would be better for these investigations, but unfortunately the authors don't know of such small cutters (with the diameter smaller than 1.00mm).

Fig. 4 — The picture of coin no. 6 after drilling with two types of cylindrical cutters.
On the picture the holes after drilling are shown.

The second problem is connected with the XRF spectrometer's diameter, which are usually smaller than 1 mm (e.g. 0.7 mm). For these reasons, in drilling practice, the 1 mm drill should be used, but a tool of

such size is very damaging for small historical objects. The other important thing is the possibility of contamination of a sample by material coming from a drill (drill tools compositions). For the main coinage alloying elements this contamination isn't dangerous, but in the analysis of traces, information about contamination is significant. Considering the facts, we can prepare samples more appropriate. One of the acceptable ways is to prepare a cross-section (in case of incomplete coins) or a small flat area on the edge of a coin (taper sectioning by grinding and polishing) (Numismatics vol. IV 1998 114). Because cutting a coin is extremely damaging for artifacts, we choose the taper sectioning method, without mounting coins in resins. The edge of a coin as well as many points located on the radius from the centre toward the edge, were investigated. The results (table 2) show that there are not big differences in the chemical composition of a coin.

Table 2 — The comparison of silver and copper concentration using different physicochemical methods.

w/w, %	Ag			Cu		
	SEM-EDX	ED-XRF	ICP-OES	SEM-EDX	ED-XRF	ICP-OES
6-2	46,73	47,17	46,455	34,67	52,63	46,568
6-3	43,89	46,56	45,365	53,26	53,24	45,892
6-4	56,81	53,70	45,461	32,61	45,94	43,244

For this reasons it was decided that the properly prepared edge of a coin could be used for our investigation. One of the proper ways of preparation is polishing with silica, alumina (corundum) or textile materials and diamond lubricants. Si-C materials don't contaminate a sample, because the spectra signals don't have an influence on quantitative results of the analysis. After four stages of grounding and polishing, the surface of a sample is excellent both for microscopic and XRF analysis.

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