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The Conservation of Early Post-Medieval Period Coins Found in Estonia

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This article deals with coins of varying consistency in silver and the problems of conserving them. The aim of the research was to find the most suitable method for the conservation of poorly preserved early post-medieval period coins with varying composition. To achieve this, first, the composition of both the metal and the corrosion products of the ancient coins were analysed, and then comparisons of experiments with different cleaning methods were carried out in order to find out the least harmful and most efficient one. A test was also performed to determine the necessity and efficiency of stabilising the surface of the coins after cleaning.

1. Introduction

The earliest hoard of coins found in Estonia dates back to the Early Iron Age (1st–5th century AD), but most of the hoards found date to the period of 1558–1611. While from the entire Middle Ages we only have information about fifty coin hoards, the turn of the 16th and 17th centuries has brought about hundreds of discoveries which contain tens of thousands of coins (Kiudsoo 2007: 3–6). This extraordinary number of hoards is primarily related to the Livonian War (1558–1583) and the Polish-Swedish Wars (1600–1629) during which large number of the inhabitants of Estonia and Livonia perished and whose meagre savings, hidden in the ground, out of fear of wars, remained there for centuries. This circumstance points to the magnitude of tragedy that beset the country, but on the other hand provides researchers with an opportunity to study abundant material (Kiudsoo 2007: 23–24). One peculiarity of the coins dating back to the Livonian War is the fact that often they only have a very thin surface layer rich in silver, while the content of silver in the bulk material is very small (even below 10%). The conservation of such coins is very complicated and it is easy to spoil them irrevocably by inept handling. The aim of this project was to develop reliable methods for conservation of debased silver coins which are poorly preserved. The coin collection of the Institute of History (IH) of Tallinn University was used as source material; cleaning methods were tested on recently excavated coins from several medieval and early post-medieval hoards. Samples were selected by the principle that all main types of coins used in this area should be represented. Coins the conservation of which does not usually cause serious problems because of the high silver content - for instance thalers and Russian wire kopecks - were left out.

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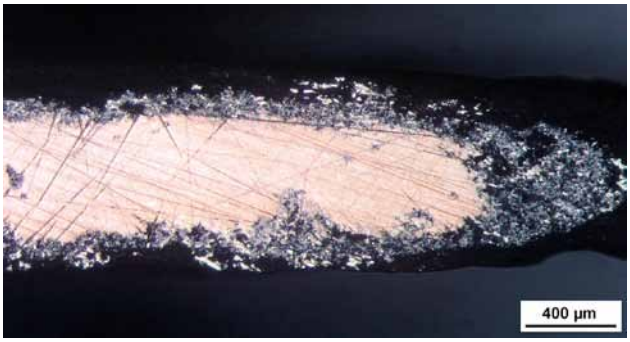

Fig. 1: Cross-section of the edge of a schilling (AI 5000, 964:24). The sparse surface layer rich in silver was formed due to selective corrosion.

2. The environment of the finds and condition of the objects

Preservation of objects in the environment is affected by a number of factors: mechanical and chemical parameters of the soil, conditions of humidity, contact with air, moving of objects (arable lands), and also the composition of the material, its homogeneity and other materials in direct contact with it, the macro- and micro-composition arising from its manufacture and finally the quality of the surface of the metal (Watkinson and Neal 2001: 1–8).

Archaeological silver (which in the case of coins may also contain a substantial amount of copper) may easily become brittle after lying in the soil for a long time. The reasons for this are changes in its microstructure caused by corrosion and long-term ageing. Although silver is generally little susceptible to corrosion, one can still come across mineralised objects that are extremely fragile. The surface of the silver may be porous and easily damaged, if copper (or another alloying element) has vanished due to selective corrosion and the object has thus acquired an 'enriched' layer of silver (**figure 1**).

In unfavourable conditions, the silver-copper alloys tend first to lose copper, leaving behind a surface layer rich in silver. Such objects are often fully covered with the corrosion products of copper, which is why they can be mistakenly taken for copper materials, if determined only by

visual observation (Watkinson and Neal 2001: 139). Even pure silver (unalloyed with copper or other elements) that has been exposed to outdoor environment for years may be damaged by aggressive corrosion caused by humid conditions and dissolved salts. The result of reaction with the latter is the formation of silver chloride, which occurs naturally as a mineral chloragyrite (formerly *cerargyrite*) and is also known as horn silver. The chloride of pure silver is white but if silver contains impurities it may be grey, brown or tarnished purple. While excavating, one should bear in mind that due to light sensitivity of AgCl silver objects may become dark. In addition to that, silver may react with bromide ions dissolved from degraded organic matter, forming silver bromide (which is also light sensitive). On silver objects buried in anaerobic conditions, silver sulfide may form when silver reacts with nitrogen sulfide produced by bacteria that reduce the sulfide (Selwyn 2004: 139).

Indoors, silver is sensitive to tarnishing, which is caused by sulfur compounds found in the air (for instance, hydrogen sulfide H_2S) or due to contact with sulfur. Since there is always a little amount of H_2S in the air, silver objects darken with time and Ag_2S forms on their surface.

Because human sweat always contains sodium chloride, handling silver objects may bring about chloride pollutants on their surface, if sweat or its residues remain on the surface of the metal. Sodium chloride reacts with silver and forms silver chloride, which is light-sensitive and will begin darkening with time (Selwyn 2004: 138).

The surface layer of archaeological copper removed from the finding location may have become coarse from corrosion products. The dominant corrosion products are cuprite and malachite; the original surface or shape of the object may have been preserved in the layer of cuprite, which remains under the copper (II) complex compound. Corrosion is accelerated by constant humidity in the ground, and also by high content of carbon, phosphates and chlorides. Corrosion process in the finding environment is also affected by increased pollutants in the air, and also by proximity to highways where chlorides are used against freezing (Selwyn 2004: 64).

Copper, as a chemically active metal can form a large number of compounds with different elements (O, Cl, S), which in archeological objects occur as corrosion products. This makes conservation of finds difficult, because even within the same area of the find the condition of objects may vary greatly due to the different concurrence of environmental variables and requires individual approach to each object, because various compounds (corrosion products) require different treatment.

3. Experiments

With the experiments conducted for this project we hoped to answer the following questions:

- What chemical compounds do corrosion products on archeological coins consist of?
- What is the elemental composition of metal of coins about to be conserved? To what extent does the metal composition differ in the nominals (with a low content of silver) that have been used and manufactured in various time periods?
- What procedures (galvanic, electrolytic, chemical and mechanical treatment) are least hazardous when conserving archeological coins?
- Which chemicals used most often for conserving silver and copper are the most effective and cause the least damage and risks?
- Is the use of laser justified in cases of coins with a low content of silver?
- Do various coatings (for instance, wax or lacquer) protect the material from damage by light?

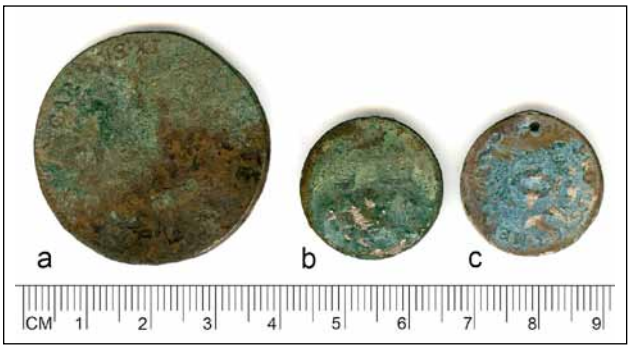

Fig. 2: Analysed coins form the Kaarma hoard: a - SM 10588:5, b - SM 10588:405, c - SM 10588:406.

3.1 Analysis of the material

Analyses of the coins were carried out in the Centre for Materials Research of Tallinn University of Technology. Out of the instrumental methods, optical microscopy, scanning electron microscopy (SEM – JEOL 840A and Zeiss EVO MA-15) together with energy dispersive x-ray microanalysis (EDS – LINK AN 9500 and INCA Energy 350) and x-ray diffraction analysis (XRD – Bruker AXS D5005) were applied.

XRD was applied for the study of three coins (**figure 2**) which originate from the Kaarma hoard (SM 10588)[1]: two 1-öre (405, 406) and one 4-mark coins (5), and also a schilling from the Otepää hoard (964:26). The result of the analysis is presented in **figure 3**. Out of corrosion products, cuprite Cu_2O was identified on all four coins and also malachite $Cu_2(CO_3)(OH)_2$ on some coins (more on the 4-mark and less on the 5-öre coins). On the 4-mark and on one 5-öre coin the greenish tint is also evidence of malachite. The blue layer of the other 5-öre coin (406, with a hole) indicates the presence of georgeite, the chemical composition of which is identical with malachite but its structure is amorphous and is therefore not visible in the XRD pattern. The width and small intensity of the peaks of malachite is also owed to its amorphous structure. EDS analysis was applied to determine the elemental composition of the coins. From the edges of the coins ~0.3 mm was ground off and the exposed surface of the cross-section was analysed. Spectra were acquired from the area of about 0.25 mm^2 (**figure 4**). In the majority of coins only the inner surface was analysed, whereas only one coin (961:12) had a clearly distinguishable structure and

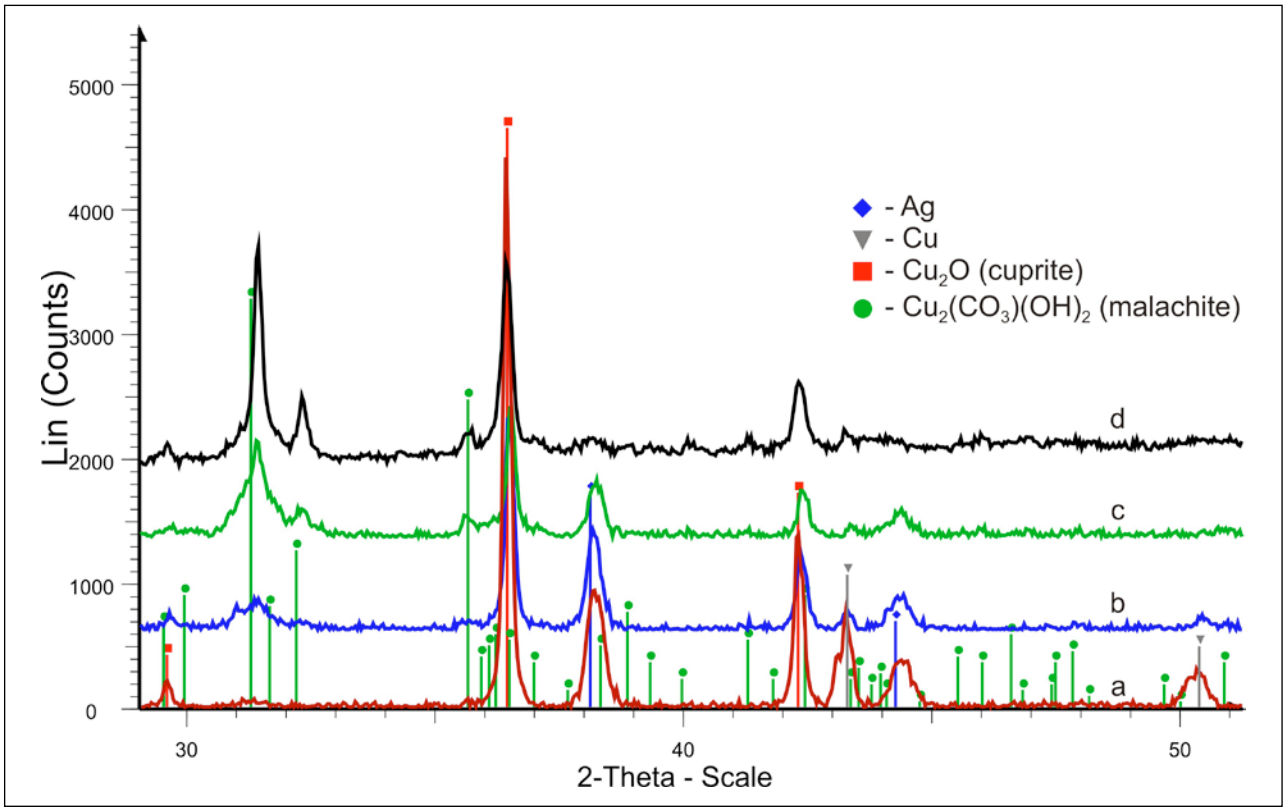

Fig. 3: X-ray diffraction pattern of coins: **a** – Otepää (946:26); **b** – Kaarma (10588:406), **c** – Kaarma (10588:405), **d** – Kaarma (10588:5).

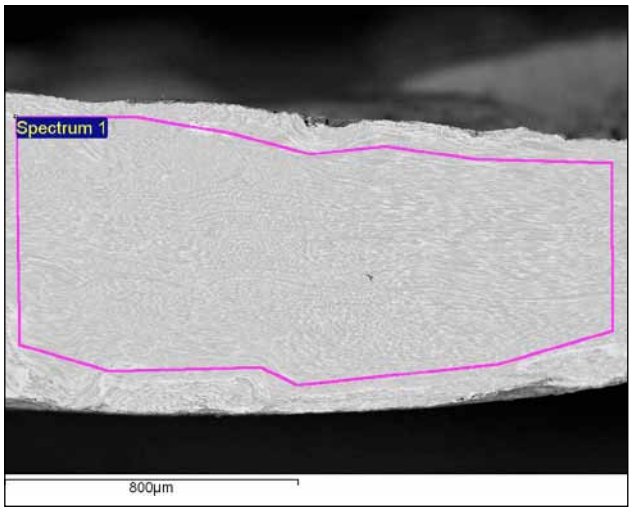

Fig. 4: Cross-section of the edge of a coin (AI6961:215) with the analysed area outlined (SEM, backscattered electron image).

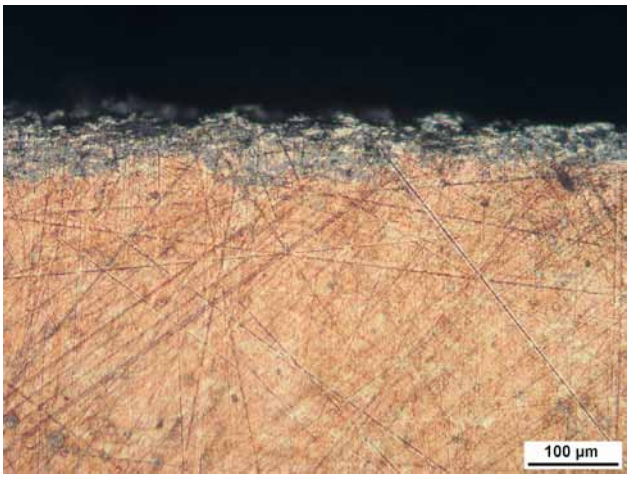

Fig. 5: Cross-section of a coin (AI 5000, 961:12). A thin layer richer in silver is distinguishable.

sufficient thickness of surface layer richer in silver that could be analysed separately (**figure 5**). The results are presented in Table 1. For simplicity, only Ag and Cu contents are given and other elements, found in some coins, are left out.

As Table 1 shows, the actual content of Ag in silver coins could vary rather greatly. Yet for a coin with a 94% content of copper to be acceptable as silver money, a technology had to be devised by means of which the surface layer of coins with a very low Ag content was given a silvery gleam. It is possible that one stage of the manufacture of coins was treating them with some acidic solution known at that time (acetic acid, tartaric acid, alum) (Hickman 1977: 84–85; Smith and Gnudi 1990: 360–361), which made copper react with it and as a more active metal, leave the surface of the coin into the solution along with its reddish gleam.

As one can see, the composition (Ag/Cu ratio) of the coins varies in quite a wide range, but some general rules can be noticed:

- The silver content of the coins does not exceed 50%.
- Some coins have more or less standard composition (Ag/Cu ratio 50/50, 40/60 or 30/70), while others are debased beyond control and may contain even less than 6% of silver.

Name of hoard	Sample ID	Ag wt%	Cu wt%	Group
Otepää (AI 5000)	964:24	13.2	86.8	B
	964:26	14.2	85.6	B
Rutikvere (AI 5000)	961:12 inner area	27.5	72.4	B
	961:12 surface layer	45.7	54.2	
	58:26	5.7	94.3	B
Kaarma (SM 10588)	403	40.5	59.3	A
	404	40.4	59.4	A
	406	49.4	50.4	A
Kuusalu (AI 7069)	1	28.9	71.1	A
	2	29.6	70.4	A
	3	33.1	66.9	A
	4	49.9	50.1	A
	5	8.1	91.9	B
	6	9.0	91.0	B
Puru (AI 7072)	1	17.8	82.2	B
	2	17.1	82.9	B
	3	17.3	82.7	B
Saaremaa (SM 10663)	1800	33.4	66.6	A
	1805	7.7	92.3	B
	1806	13.6	86.4	B
	1809	6.6	93.4	B
	1820	47.3	51.7	A
	1821	8.0	91.4	B
Linnakse (AI 6961)	215	40.9	48.3	A
Padise*	HMK:467	18.7	81.3	B
	HMK:477	40.9	59.1	A
	HMK:478	20.5	79.5	B
Harju-Risti*	HRP:101	12.5	87.5	B
	HRP:102	13.3	86.7	B
	HRP:103	7.6	92.4	B
Kurna*	KRN:01	29.1	70.9	A

Table 1: Composition of analysed coins analysed with EDS grouped according to Ag content in group A (Ag content over 30%) and B (Ag content below 30%) (last column). The coins found in Padise, Harju-Risti and Kurna are recently excavated and, as they are currently under identification-registration process, they have so far only temporary ID numbers.

Experience has shown that with coins containing 30% or more silver, there are usually little, if any, serious conservation issues, while the lower-content pieces are highly sensitive to improper handling. So, from a conservators' viewpoint, coins can be classified into two groups:

A - silver content 30% or more
B - silver content below 30%

Hereinafter, coins used in the current experiment are marked as group A or B, according to their composition.

3.2 Conservation methods of archaeological coins

Coin hoards can contain hundreds, or even thousands of coins, which have to be identified by numismatists. The surface of coins and their legends are often hidden below corrosion products and burial deposits. Coin hoards must be treated with an efficient and non-damaging way in order to reveal the surface legends and produce coins that are stable in the museum environment.

When a collection of recently excavated coins, often covered with dirt or corroded together, is delivered to the conservation laboratory, it is not easy to distinguish whether their alloy is predominantly silver, copper, or

whether it contains any other impurities. The simple laboratory tests may also not be of help, for these are mostly based on the reaction of the surface layer of the coin and may therefore yield misleading results. Hence, although handling of silver itself is generally less critical than of other metals, there may be a considerable amount of copper in a seemingly silver object. If one is not sure about the composition of the metal and does not know whether it contains more silver or copper, it is safer to treat it as copper (Hamilton 1999: 304).

Within this experiment, it was decided to try out some of the conservation procedures found in literature and determine based on the results their suitability for the conservation of coins found in hoards of the early post-medieval period. Coins with lesser numismatic value from several hoards and finds were used as trial objects. Emphasis was on chemical methods as the large amount of material to be conserved in a typical coin hoard makes it difficult to treat coins individually by hand. In the lit-

Fig. 6: Galvanic cleaning with aluminium granules in sodium carbonate solution. Group A coin – SM10663:1800, B – HRP:102. Additional treatment - sodium tiosulphate solution.

Fig. 7: Galvanic cleaning with aluminium granules in alkaline Rochelle solution. Group A coin – SM10663:1820, B – SM10663:1821.

Fig. 8: A coin from group B (SM10663:1821) coated with a layer of copper in the course of galvanic cleaning.

erature, treatment times as long as several weeks, or even months with some cleaning methods, are sometimes suggested. In the current experiment the treatment time was more limited and if there was no visual improvement in the corrosion in 2–3 days, the experiment was terminated and cleaning was completed with another, more efficient method.

3.2.1 Galvanic cleaning

Description: In an electrolytically conducting solution, the artefact is brought into contact with a piece of less noble metal - usually aluminium or zinc. While the sacrificial anode metal corrodes, the opposite process - reduction of the corrosion products - occurs on the artefact, and the corrosion layer decomposes. Aluminium is usually used in the form of foil (galvanic wrap) or granules. The object is left in the solution until the aluminium is oxidised and the process is repeated until the desirable result is achieved. This method can be applied, if the metal core of the object has been preserved (Hucke and Bleck 1983: 36–40; Rodgers 2004: 85; Doménech-Carbó *et al.* 2009: 135–136).

Experiment: Two experiments were conducted with different solutions - one with 10% of sodium carbonate (washing soda) and another with alkaline Rochelle solution (a mix containing 5% of sodium hydroxide and 15% of potassium sodium tartrate) as the electrolyte. Aluminium granules were used as the anode. In the solution of sodium carbonate the coins were kept up to 72 hours (3 days), after every 24 hours the condition of the coins was checked and the solution was changed. In the alkaline Rochelle solution an active reaction started immediately between NaOH and the Al granules with the emission of a gas with a pungent odour. The experiment lasted 30 minutes.

Result of the experiment with sodium carbonate: During the first 48 hours, the corrosion was partially removed (on both A and B group coins), after that, no visible changes were noticed (**figure 6**). Electrochemical corrosion of the aluminium granules still continued after 48 hours - the granules adhered on the coin's surface and white sediment appeared - but no more corrosion products were removed from the coins. Both A and B group coins needed additional treatment (12h in sodium tiosulphate solution) to remove the tarnish completely.

Result of the experiment with alkaline Rochelle solution: In the course of the treatment, the coins were covered with a dark but easily washable layer. Under this layer a copper-red surface (group B) or salmon-pink stains (group A) appeared (figures 7, 8). The obvious reason for this is the fact that the corrosion products of copper had predominated on the surface of the coins (especially in the case of group B coins), which were then reduced to elemental copper. The surface of the coins was therefore distorted.

Conclusion: The galvanic method with sodium carbonate is not harmful for the coins, but it is not very effective either (or requires very long treatment time). Galvanic cleaning with alkaline Rochelle solution (or other solutions containing NaOH) is unsuitable for silver-copper alloys (for both A and B group coins in the current experiment), because the process cannot be controlled and a layer of copper adheres to the surface of the coins.

3.2.2 Electrolytic cleaning

Description: Electrolytic cleaning of silver takes advantage of the reducing action of electrolysis, which removes the chloride and sulphide ions from silver chloride. By use of direct current, the negatively charged ions move over to the positively charged anode, separating chlorine as gase-

ous or being oxidised to sulphates. In the course of the process, silver that had become a part of corrosion products, is reduced back to metal, which emerges as granules or a layer weakly attached to the main material. Different chemical solutions such as 5–30% formic acid (HCOOH), 2–15% sodium hydroxide (NaOH) or 2–5% sodium carbonate (Na_2CO_3) are suggested as electrolytes (Hamilton 1999: 304; Doménech-Carbó *et al.* 2006: 137). After electrolysis, objects have to be rinsed with distilled water; in case of a basic electrolyte, rinsing has to be quite intensive in order to avoid the forming of a white deposit on the surface of the object. Then, the object has to be dried with hot air or dehydrated in acetone (Hucke and Bleck 1983: 36–40; Dedik 1989: 96).

Experiment: Three experiments were performed, where 5% formic acid was used as electrolyte in the first, 2% NaOH in the second and 5% sodium carbonate in the third one. In all cases, stainless steel was used as anode; direct voltage applied was 3–5 V. In case of the solution of formic acid, amperage was relatively low (~100 mA), in the case of NaOH and Na_2CO_3 amperage was higher (~1 A and ~400 mA respectively).

The result of the experiment with formic acid: In two hours the coin was cleaned from corrosion products, but acquired a reddish tint (**figure 9**). Since formic acid is itself an active chemical agent, the effect of electrolysis is unclear (apart from depositing copper stains on the surface).

The result of the experiment with sodium hydroxide: Because of an active separation of gases from the surface of the coin, it was decided to stop the experiment after 50 minutes, although all corrosion products (some greenish speckles of malachite) had not yet been separated. After the coin was washed, it appeared that its entire surface was turned to copper-red (**figure 10**).

The result of the experiment with sodium carbonate: After 3–15 minutes the corrosion layer was softened enough to allow the cleaning of the surface with a toothbrush. The coins looked clean and shiny, but both A and B group coins had acquired a yellow, brass-like tint (**figure 11**).

Conclusion: Electrolytic cleaning is a quite effective method for removal of the corrosion layer, but like galvanic treatment, it cannot be recommended for silver artefacts, alloyed with copper (i.e. most of post-medieval silver coins), because there is always a risk of plating a layer of elemental copper on the surface. In the case of copper coins, for instance, electrolytic cleaning should be perfectly usable.

Since both galvanic and electrolytic cleaning resulted in silver coins with yellow or reddish tint, we had to find a way to get rid of the copper layer. For this purpose, a solution of sodium persulfate was used which, as an active oxidant, is also used for etching copper off from printed circuit boards. Some sources (Nikitin and Melnikova 2002: 173) also suggest potassium persulfate for 'whitening' silver-copper alloys. After the removal of copper from the surface, the silvery appearance of the coins was restored (additional treatment in figures 9 and 10). Sodium persulfate is a very active chemical agent and using it on archaeological artefacts is clearly in contradiction with

Fig. 9: Electrolytic cleaning of a group A coin (SM10588:404) in 5% solution of formic acid. Additional treatment - sodium persulfate solution.

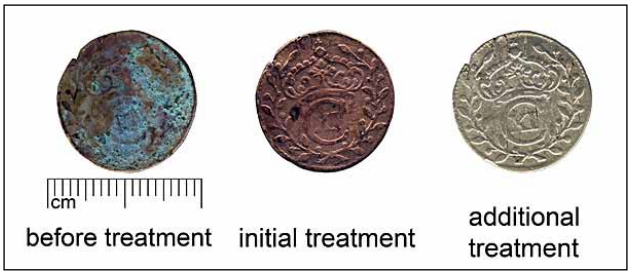

Fig. 10: Electrolytic cleaning of a group A coin (SM10588:490) in 2% solution of sodium hydroxide. Additional treatment - sodium persulfate solution.

Fig. 11: Electrolytic cleaning of group A (AI 7069:3) and B (HRP:103) coins in sodium carbonate solution.

Fig. 12: Cleaning of a group A coin (SM10588:754) with 10% solution of ammonia for 6 and 24 hours (lower and upper half of the coin). Additional treatment - formic acid solution.

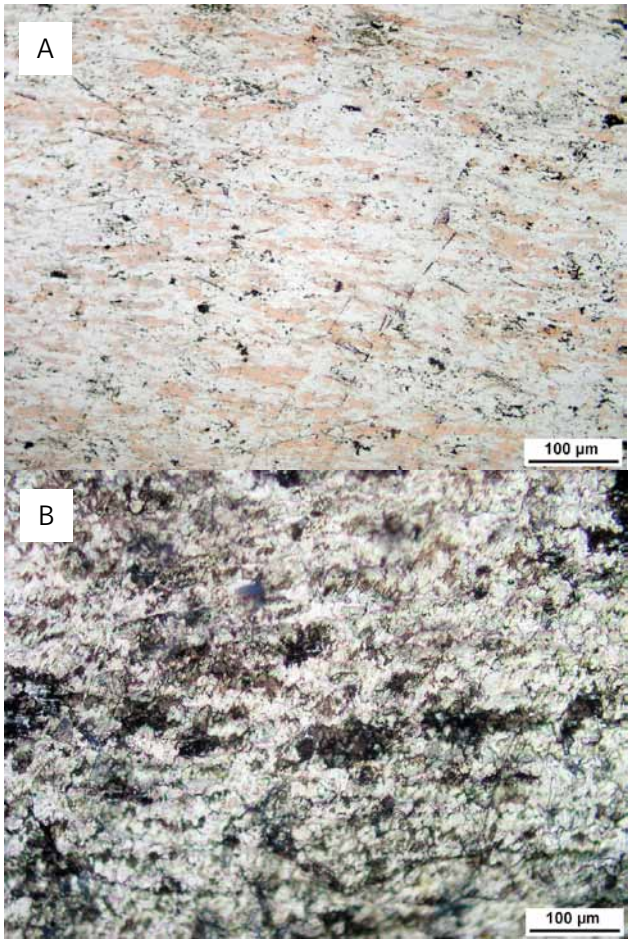

Fig. 13: Surface of a newly minted sample coin of group B (94% Cu - 6% Ag) before (**a**) and after (**b**) treatment with a solution of ammonia.

Nikitin and Melnikova 2002: 128–129, 172–173; Rodgers 2004: 107–119). Usually, silver and copper are dealt with separately, which is why the presented formulas and recommendations have to be taken with a reasonable caution. In the specialised literature, solutions based on organic acids, EDTA and ammonia are mostly recommended.

Ammonia: Many formulas for cleaning silver contain ammonia, but with archaeological coins the term *silver* must be taken 'with a grain of salt', because often the main component of the material is copper. Ammonia is dangerous for copper because oxygen present in the air reacts with copper and causes corrosion. With the alloys of silver and copper the use of ammonia has to be regarded with the greatest caution (Nikitin and Melnikova 2002: 130).

Experiment: An archaeological coin (group A, SM10588:754) was treated in a 10% solution of ammonia for 6 and 24 hours; and, a comparative experiment was performed in the same conditions with new, specially made sample coins with silver content of 50% and 6% (group A and B).

Result: In 24 hours, not all corrosion products were separated from the coin, but the surface of the metal had become very porous (**figure 12**, initial treatment, upper half of the coin). To save the artifact from further damage, final cleaning was performed with formic acid solution (**figure 12**, additional treatment). A newly-minted, group B sample coin was damaged by becoming tarnished and porous (**figure 13**). The surface of a group A coin remained visually unchanged.

Fig. 14: Cleaning of group A (SM10588–928) and B (AI7072:2) coins with 10% solution of acetic acid. Additional treatment of coin A - formic acid solution.

Conclusion: The solution of ammonia cannot be recommended for cleaning archaeological silver coins, because most of them are alloyed with copper and ammonia damages the structure of the surface of coins by reacting with Cu.

Acetic acid: Acetic acid is a relatively weak acid, which is why separation of corrosion products is slow (it may take days or even weeks). For this reason, however, the process is easily observable and entails minimal risk (Nikitin and Melnikova 2002: 130).

Experiment: Archaeological coins from groups A and B were treated with a 10% acetic acid solution from 3 to 24 hours.

Result: In 6 hours a blue, surface corrosion layer was separated from a group A coin. In 24 hours the rest of the corrosion products separated only partially and final cleaning was performed with formic acid solution. The group B coin was cleaned completely in 3 hours (**figure 14**).

Conclusion: The procedure may be recommended for cleaning both A and B group coins but one should consider the time-consuming nature of the treatment in case of thicker corrosion layers.

Formic acid: Formic acid is the strongest organic acid, which is why it is also very effective as a cleaning agent for archaeological coins. Separation of most corrosion products and burial deposits takes place quite quickly (usually in 1–3 hours). Some corrosion products, however, may need longer treatment; in most cases a positive result is more or less guaranteed. In the British Museum, 30% formic acid solution is also used for removing cuprite corrosion from debased silver coins (Thickett and Enderly 1997: 185). In the current experiment it was not a coincidence that, in case of insufficient effect of less active chemicals, additional treatment was mostly (and successfully) applied with formic acid solution. Due to the pungent odour and irritating effect, any handling of formic acid should be conducted under a fume hood and contact with skin should be avoided (Dedik 1989: 97).

Experiment: Archaeological coins of group A and B were held in 10% formic acid solution from 30 minutes to 24 hours.

Result: The coin from group B needed only 30 minutes for complete cleaning. The group A coin took 6 hours to be treated due to thicker layer of cuprite/malachite corrosion. The coin from group A was kept in formic acid solution for 24 hours, but no visible damage on the surface of the coin was detected (**figure 15**).

Conclusion: Formic acid is a very effective chemical agent and a 5–10% solution can be recommended for cleaning both group A and B coins. However, as it is always wise to start with less aggressive chemicals and move 'up', if necessary, formic acid should never be the first choice. It is not recommended to keep group B coins in formic acid solution for more than 24 hours as some damage of the metal surface may occur according to our experience.

Fig. 15: Cleaning of group A (SM10588–927) and B (AI7072:1) coins with 10% solution of formic acid. Treatment of coin A - 24h, B - 30 min.

Ethylenediaminetetraacetic acid

Ethylenediaminetetraacetic acid (EDTA, Trilon B) is also a component of many solution formulas for cleaning silver. The solution also works effectively for removal of a thick layer of corrosion; the process is well observable and can be stopped, if necessary. In specialis§ed literature, one may still come across warnings that EDTA solution may damage the surface of the metal (Nikitin and Melnikova 2002: 172–174).

Experiment: A 10% EDTA solution was used and coins (A and B group) were held in it for up to 24 hours.

Result: The group A coin (SM10588:338) was treated in EDTA solution for 6 and 24 hours (**figure 16**, lower and upper half of the coin respectively). In 24 hours, corrosion products had separated from the surface of the coin but instead, a yellowish layer, that was hard to dissolve, appeared on the surface. The coin needed additional treatment with formic acid solution. The group B coin (AI7072:3) was completely cleaned just in 30 minutes without any side-effects (**figure 16**).

Conclusions: Apparently, efficiency of the EDTA solution depends on the thickness and composition of corrosion products – the thinner layer on the group B coin was removed quickly while the thicker, cuprite-malachite corrosion on the group A coin needed more time. Additionally longer contact with EDTA caused yellow coloration on the coin's surface. Hence, EDTA solution can be used for cleaning both A and B group coins, but the treatment time is limited - if corrosion products are not removed or softened enough in 2–3 hours, cleaning must be continued with another chemical agent.

Fig. 16: Cleaning of group A (SM10588:338) and B (AI7072:3) coins with 10% solution of EDTA. Additional treatment of coin A - formic acid solution.

Ammonium tiosulphate and sodium tiosulphate

Ammonium tiosulphate and sodium tiosulphate have been used for treatment of archaeological silver artefacts for decades. Both are also used in photography as fixing agents. The role of fixers in photography is to remove unexposed silver halides from the image by transforming them to water-soluble complex compounds, which can be easily washed out. The same complexing reactions are applied for the removal of insoluble halides and sulphides from the surface of archaeological silver (Cronyn 1990: 233; Nikitin and Melnikova 2002: 174). Ammonium tiosulphate is able to dissolve even the almost insoluble silver sulphide layer (Selwyn 2004: 137) and is used on regular basis for removal of silver chloride deposits (Ghoneim and Megahed 2009: 149). In some cases, however, ammonium tiosulphate has been reported to work insufficiently (Lowenstam *et al.* 1987: 8) and to have a tendency to etch the surface of already clean silver (Boyd and Mango 1992: 85). In debased silver coins found in earth, horn silver is

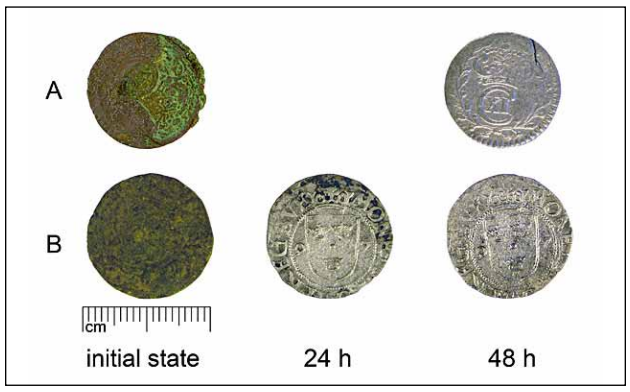

Fig. 17: Cleaning of group A (AI7069:2) and B (HMK:467) coins with 30% solution of sodium tiosulphate.

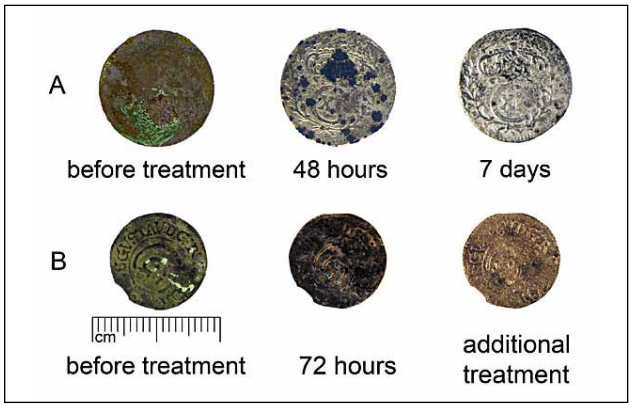

Fig. 18: Cleaning of group A (AI7069:1) and B (AI7069:5) coins with 9% solution of thiourea. Additional treatment - electrolysis in sodium carbonate solution.

Fig. 19: Cleaning of group A (HMK:477) and B (HRP:101) coins with alkaline dithionite. Additional treatment - formic acid solution.

rarely a main issue as the soil is poor in chlorides and corrosion products of copper are usually dominating. In conservation practice, ammonium tiosulphate is usually used because of its faster action, but sodium tiosulphate can be applied instead as well. To compensate the slower action of sodium tiosulphate the solution must be stronger - usually 15% ammonium tiosulphate or 30% sodium tiosulphate solutions are used.

Experiment: Two coins (group A and B) were treated in 30% sodium tiosulphate solution for 24 and 48 hours, an additional (not archaeological) group A coin was held in the solution for seven days to verify the claim of etching of the metal surface.

Results: In 24 hours corrosion products were partially removed from the surface, but in 48 hours both A and B group coins were completely cleaned without any visible damage to the metal surface (**figure 17**). After one week in the solution the surface of a group A coin had no signs of etching, however, a thin purple layer was formed onto the surface that was difficult to remove.

Conclusions: Ammonium and sodium tiosulphate solutions can be recommended for cleaning both A and B group coins, but the pieces should not be kept in the solution longer than necessary (48 hours is usually enough). After treatment coins must be rinsed properly, otherwise yellow stains may appear on the surface after drying.

Thiourea: Thiourea (SC(NH2)2) is another complexing agent that can be used for the removal of corrosion products (Selwyn 2004: 137). As compared with ammonium or sodium tiosulphate, thiourea is a weaker reagent and therefore treatment may take longer time. Sometimes thiourea is used combined with organic acids (Plenderleith and Torraca 1968: 246; Al-Saad and Bani-Hani 2007: 178). In jewellery, solutions called 'acidified thiourea' are well known as tarnish removers. Such solutions can also contain oxidising (phosphoric or sulphuric) acids. Thiourea can cause eyes and skin irritation and is also suspected as a carcinogen.

Experiment: Coins from groups A and B were treated in 9% solution of thiourea in water-ethanol mixture (30% ethanol was added because of poor solubility of thiourea in the water).

Results: On the group A coin, dissolution and softening of the corrosion layer took place, but very slowly - complete cleaning took seven days. On the group B coin, the corrosion layer was removed in 72 hours, but a dark layer, like artificial patina, was formed on the surface instead (**figure 18**). The layer was insoluble in formic acid solution, but it was eventually removed by electrolytic treatment in sodium carbonate solution. After removal of the dark layer, the surface of the coin appeared copper-red.

Conclusions: Thiourea has indeed some cleaning capability, especially on group A coins, but because of its toxicity and tendency to form a dark patina layer on group B coins, there is very little reason to use it for cleaning archaeological silver coins.

Alkaline dithionite: Alkaline dithionite method is another approach that was originally developed for silver finds in saltwater sites (MacLeod and North 1979: 165–170). The basic idea - decomposing the corrosion layer by reducing corrosion products to metallic silver - is the same as in electrolytic and galvanic treatment, but instead of electric current a chemical reducing agent - sodium hydrosulphite ($Na_2S_2O_4$, also called sodium dithionite) - is used. The alkaline dithionite treatment has been a very effective way of cleaning silver coins and separating silver objects that are encrusted together (Hamilton 1999: 305).

However, as the reducing agent is able to also reduce copper (the same treatment is applied for copper and bronze artefacts (Scott 2002: 371)), there is possible risk of copper plating on coins, just as with electrolytic and galvanic cleaning, because debased silver coins are coated mostly with copper corrosion.

Experiment: Coins from groups A and B were treated in alkaline dithionite solution (4% sodium hydroxide + 6% sodium hydrosulphite) for 6 to 48 hours. During treatment, the container was full of solution and tightly sealed to avoid oxidation of sodium dithionite.

Results: The group A coin (HMK:477) was partially cleaned after 6 hours and completely cleaned after 24 hours of treatment without any visible side-effects (**figure 19**). The group B coin was only partially cleaned and it was decided to terminate the experiment after 48 hours of treatment because between 24 and 48 hours there were no changes in corrosion stains. The coin needed additional treatment with formic acid solution (**figure 20**).

Conclusions: Alkaline dithionite treatment can be used for cleaning both A and B group coins, but apparently the corrosion-decomposing effect of the agent depends on the thickness and composition of the corrosion layer. The dithionite treatment works well on general corrosion, but it has trouble with heavy cuprite corrosion and it is also unable to dissolve calcific burial deposits. There are also certain limitations with handling the solution (risk of oxidation). Therefore, in the context of post-medieval silver coins found in the ground, the alkaline dithionite treatment has no real advantages over other cleaning methods.

Alkaline Rochelle: Alkaline Rochelle solution has been used in the British Museum during the last 50 years for cleaning copper and silver coins as alkali treatments are believed to be less aggressive towards alloys with a high copper content than acid-based chemicals (Thickett and Enderly 1997: 183, 189). The solution used in the British Museum contains 5% of sodium hydroxide (NaOH) and 15% of potassium sodium tartrate ($NaKC_4H_4O_6$, also known as Rochelle salt and food additive E337). Separation of corrosion products takes place quite quickly - the treatment time is usually 30 minutes. Because of sodium hydroxide the solution is a strong alkali and it must be handled with protective equipment (rubber gloves, safety clothing).

Experiment: Archaeological coins from group A and B were treated in the alkaline Rochelle solution for up to 24 hours.

Results: The group A coin was partially cleaned in 24 hours - most of the corrosion was separated, but a thin purple layer remained which was removed later with sodium tiosulphate solution. On the group B coin most of the cleaning process occured during the first 30 minutes, but the brown corrosion stains (cuprite) did not dissolve or soften and it was decided to stop the experiment after 6 hours. Cleaning was completed with formic acid solution.

Conclusion: The alkaline Rochelle salt can be recommended for cleaning both A and B group coins - the solution is not harmful to the coin metal and general corrosion is separated quickly. However, coins with cuprite corrosion may need additional treatment.

Sulphuric acid: Specialised literature does not usually suggest strong mineral acids as cleaning agents for archaeological objects. Commercial dips containing oxidising acids are also believed to be too powerful for archaeological silver (Cronyn 1990: 233). This becomes obvious considering chemical activity and the dangerous nature of the mineral acids. However, in the British Museum 5% solution of sulphuric acid is used for removal of heavy cuprite corrosion from archaeological silver coins (Thickett and Enderly 1997:185). In jewellery, whitening the surface of silver-copper alloys with solution of sulphuric acid is a common routine (Nikitin and Melnikova 2002: 173). In this work, we decided to try out concentrated sulphuric acid on one coin from group A in order to remove a thick and hardly soluble layer of malachite.

Experiment: The coin was immersed in a 72% sulphuric acid solution three times for 10 minutes each time, removing the remains of corrosion products from its surface in the meantime and making sure that the surface of the coin had not been damaged.

Fig. 20: Cleaning of group A (KRN:01) and B (SM 10663:1809) coins with alkaline Rochelle salt. Initial treatment of group A coin - 24 hours; additional treatment - sodium tiosulphate solution. Initial treatment of group B coin - 6 hours; additional treatment - formic acid solution.

Fig. 21: A coin from group A (SM10588:877) before (**a**) and after (**b**) treatment with sulphuric acid.

Result: It was possible to remove the corrosion products without damaging the surface of the coin, whereas the pink speckles, rich in copper, also disappeared (**figure 21**).

Conclusion: Concentrated sulphuric acid is certainly not a means that could be recommended for cleaning coins, for it is too risky for both the material and the conservator. Sulphuric acid may be tried only in extreme cases for group A coins as a 5–10% solution.

3.2.4 Mechanical cleaning

A variety of brushes, abrasives and hand tools are applied in mechanical methods of cleaning. According to some authors (Cronyn 1990: 64; Ghoneim and Megahed 2009: 148), mechanical methods must be preferred whenever possible because they are controllable and do not involve aggressive chemicals. However, removing the corrosion crust piece-by-piece under the microscope is very time- and labour-consuming and is not considered as an option for hoards with numerous coins.

Nevertheless, some mechanical means are usually applied in the cleaning procedure of almost every coin. The simplest one might be rubbing coins with wet paste of baking soda (sodium bicarbonate), using fingers and

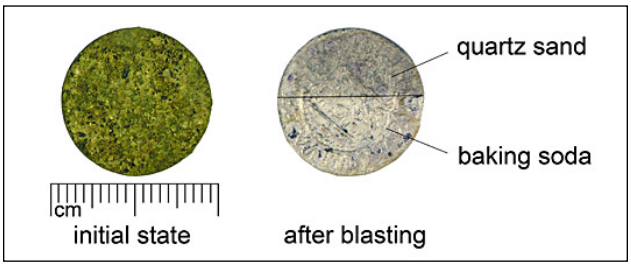

Fig. 22: A silver coin (AI7069:4) before and after microblasting.

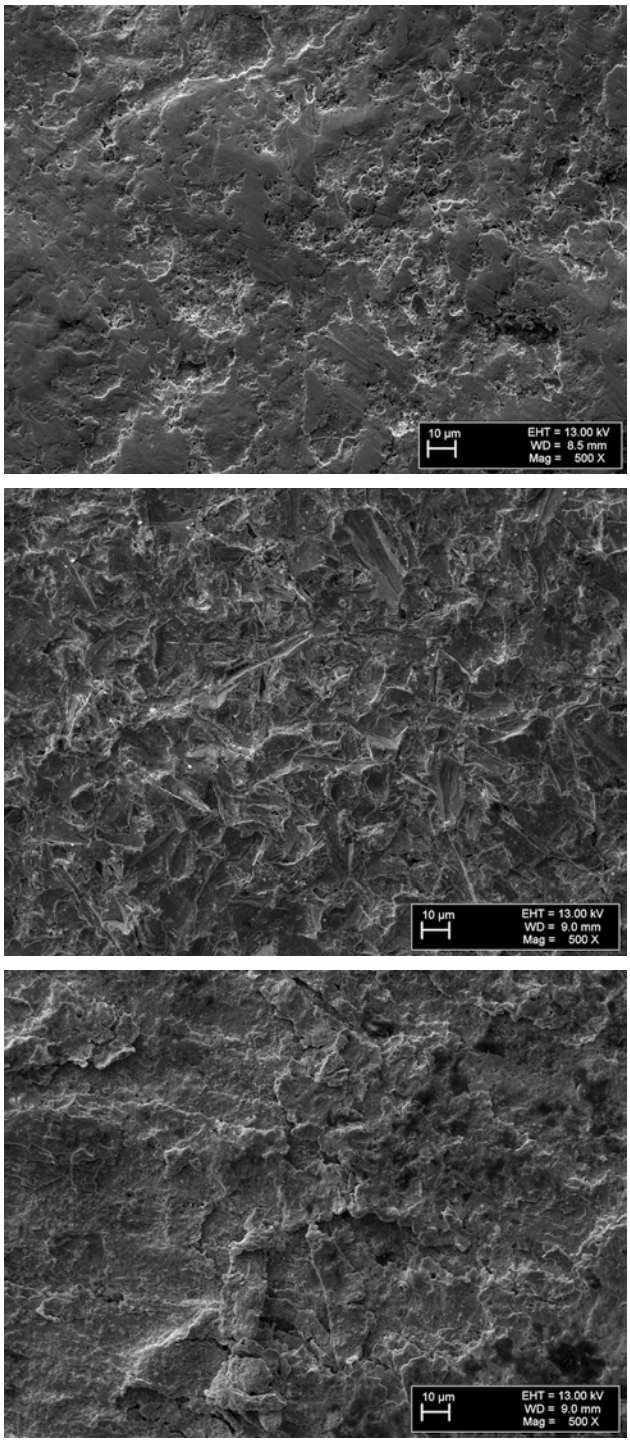

Fig. 23: The surface of the coin in SEM: after chemical treatment (**a**), after blasting with quartz sand (**b**), after blasting with baking soda (**c**).

nylon brush (hard toothbrush works well). If there is only dirt or little corrosion on the coins, a simple treatment with soda paste can be sufficient and no chemical agents are needed. In most cases some mechanical intervention is necessary after (electro)chemical methods, because the corrosion layer is usually only softened by the chemical processes, but not entirely removed from the surface.

Cleaning with wet baking soda is effective, because its particles are not hard enough to scratch the metal surface, but are still abrasive enough to remove the softened corrosion products. Mild alkalinity of dissolved sodium bicarbonate also favours the cleaning process and helps to neutralise the surface of the coins after treatment with acidic agents. In the current series of experiments, gentle rubbing of the coins with paste of baking soda was always performed after chemical, galvanic and electrolytic treatments.

The cleaning of coins with the help of various metal brushes has formerly been quite widespread. However, such a cleaning method is totally inadmissible because it irrevocably damages the surface of the coins. The layer of corrosion may often be as strong, or even stronger, than the surface layer of the metal damaged by this corrosion. The brush does not distinguish between them and removes both. On top of all, if a brass brush is used, an unnaturally golden tint adheres to the surface of the coin. Therefore, we did not try cleaning coins with metal brushes.

A more modern method of mechanical cleaning is treatment by means of a sand blaster (microblasting), where cleaning agents are abrasive particles accelerated by compressed air. In this study, we tried to clean a corroded coin with a blaster in order to determine in which cases its use might be justified and how extensive the damages on the surface were.

Experiment: An archaeological coin from group A (AI7069:4) was cleaned with blaster Dentalfarm Micra 2, using two different abrasives – half of the surface with quartz sand (180–120 mesh) and the other half with baking soda; air pressure was 3.2 bar.

Result: During the process, it was difficult to precisely define the area of cleaning (the contour left by the sand jet on the surface of the metal is diffusive). Therefore, a precise local cleaning is impossible by use of the blaster.

The blaster removed the corrosion layer with both abrasives, but the differences in the appearance after cleaning were clearly visible: the surface left by quartz sand looks darker and rougher compared to the sodium bicarbonate-blasted area (**figure 22**). When one compared the coin surfaces by use of SEM, the reasons became evident – by blasting with quartz sand, the original surface of the coin was totally destroyed, consisting only of sharp-edged impact craters from the sand particles (**figure 23b**). EDS analysis also revealed the presence of aluminium in the surface layer, indicating that some splinters from the quartz particles (Al_2O_3) were embedded into the surface. Blasting with baking soda caused less damage, but the surface was still rougher than it was after chemical treatment (**figure 23a, c**). Some delamination of the surface layer also occured.

Conclusion: Cleaning coins by microblasting hard abrasive (silica or quartz sand) is totally unacceptable as it damages the metal surface irreversibly - especially in the case of group B coins with very thin silver-rich surface layer. Blasting can be considered as an alternative to chemical methods only when it uses softer abrasive (such as baking soda) on group A coins.

3.2.5 Laser cleaning

The idea to use the energy of a laser beam to clean the surface of archaeological metal dates back to the late 1970s and has been thoroughly researched by now (Pini *et al.* 2000; Drakaki *et al.* 2004). Laser cleaning is in some sense analogous to mechanical cleaning, where the surface of the metal is influenced by use of force from outside in order to remove the layer of corrosion and grime. With laser, radiation, concentrated in a small spot, is absorbed by the corrosion layer causing its instant evaporation. The greatest advantage to mechanical cleaning is the absence of mechanical contact with the cleaned surface – all the energy is transferred by a light beam, the force of which can be widely varied. This allows the removal of corrosion products without damaging the surface itself. In many cases it is also possible to achieve adequate selectivity of the cleaning process, so that no damage of the already cleaned surface can occur. If so desired, the process can be immediately stopped (Koh 2006: 11–12).

Experiment: Two types of laser were tried to clean the surface of coins –carbon dioxide laser (*TEA CO_2 laser*) with a wavelength of 10.6 μm and neodymium laser (*Nd:YAG laser*) with a wavelength of 1064 and 532 nm. The power of the CO_2 laser impulse was increased step by step until energy density reached 96 J/cm^2. The Nd:YAG laser was tested with energy density up to 6 J/cm^2 (with 1064 nm). Two coins - one of group A (AI6961:215) and one of group B (AI7069:5) - were tested.

Result: The TEA CO_2 laser impulse did not remove the corrosion products even when it was used at maximum energy density; the Nd:YAG laser, however, had a cleaning effect in both 532 and 1056 nm modes. At both wavelengths it was possible to remove the outer thicker layer of the corrosion products, but the thinner layer of cuprite, coating the surface of the group B coin, posed a problem: it was impossible to remove it even by use of maximum energy density (**figure 24**). For the removal of the thicker layer of corrosion the operating mode at medium power (2–3 J/cm^2 with 532 nm and 5–6 J/cm^2 with 1064 nm) was sufficient. The surfaces of both cleaned coins were studied under SEM (**figure 25**). It was revealed that they were quite similar at the microscopic level, consisting of droplets melted and hardened again.

Conclusion: Laser is not a very suitable means of cleaning the surface of coins. It is unable to remove the thin layer of cuprite on the surface of group B coins; the coins of group A can be cleaned down to the metal surface but the laser impulse damages the surface of the coin by locally melting the surface layer. In addition, the method is quite labour-consuming and expensive.

Fig. 24: Coins of group A (AI6961:215) and B (AI7069:6) before and after partial cleaning with Nd:YAG laser.

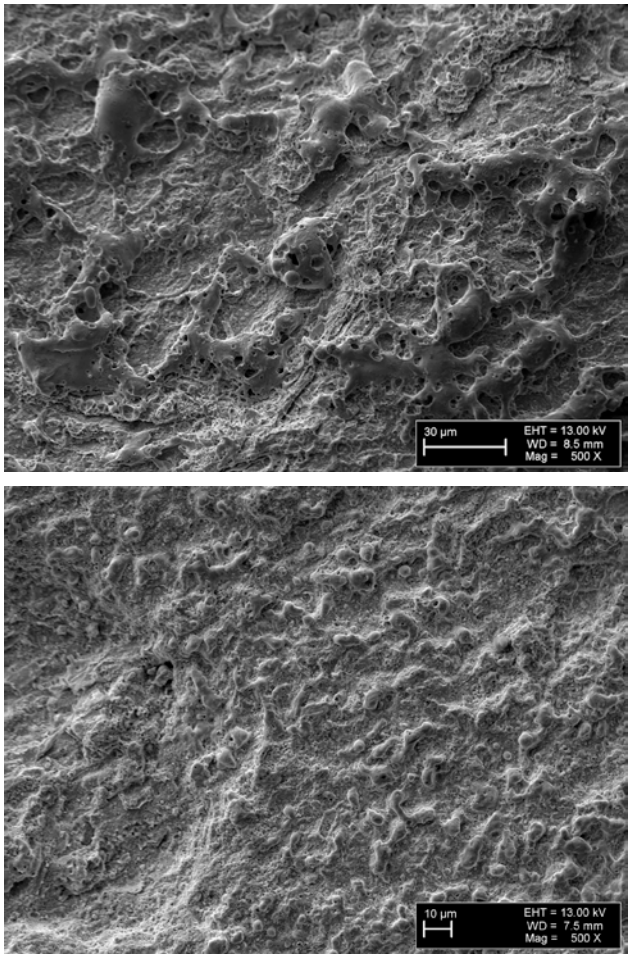

Fig. 25: The surface of group A (AI6961:215) and B (AI7069:5) coins in SEM after cleaning with Nd:YAG laser.

3.2.6 Differences in the visual appearance of the coins

The main principle for choosing a suitable cleaning method is indeed the long-time stability of the artefacts in the museum environment rather than aesthetical aspects. However, it is worth mentioning that using different cleaning agents and methods leads to different visual appearance of the coins. During the experiment, coins with similar initial state (same type of coins from the same hoard) were subjected to different treatments

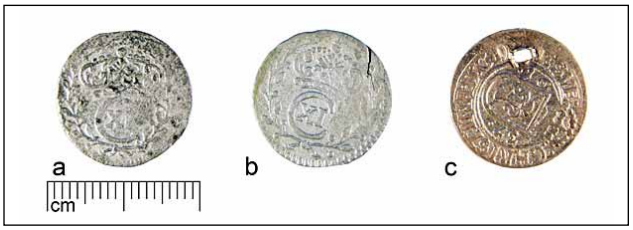

Fig. 26: Coins of group A from the same hoard after different treatment (a - AI7069:1, thiourea solution; b - AI7069:2, sodium tiosulphate solution; c - AI7069:3, electrolysis in sodium carbonate solution).

which resulted to quite different-looking coins. In **figure 26** there is comparison of three group A coins of the same type (Swedish 1-öre) from the same hoard, after different cleaning treatment. As seen, treatment with thiourea and sodium tiosulphate has given coins more or less natural appearance (as one would expect from silver coins), while electrolytic treatment has turned the coin more shiny, but with strong yellow tint.

In **figure 27** five group B coins from the same hoard are compared after different treatments. As it can be seen, treatment with alkaline Rochelle salt and formic acid solution has given quite similar results - the colour is neutral grey without any shade, but the surface looks matte. The coin, cleaned with sodium tiosulphate is also neutral in colour, but the surface looks more bright and shiny. Electrolytic treatment in washing soda solution left a yellow tint and galvanic cleaning in alkaline Rochelle solution turned the coin entirely copper-red. Of course, comparing the coins in such way is not very scientific, because the initial state of the coins is not 100% identical as corrosion in every single coin is somewhat different even within the same find. However, it shows that different cleaning methods and solutions can give visually different results and that the coins of group B are quite sensitive to variations in the cleaning process.

3.2.7 Stabilisation of the surface of coins

In specialised literature, recommendations can often be found for use of various surface coatings, like wax and lacquer, against the tarnishing of copper and silver (Hamilton 1999: 305; Nikitin and Melnikova 2002: 183–184; Selwyn 2004: 137). Practice has proved that there can be different opinions about waxing and lacquering. These surface coatings slow down but they do not stop tarnishing and corrosion of artefacts, if they happen to be in an unfavourable environment, and the material the surfaces are coated with, keeps aging as well. If such an object needs to be cleaned and conserved again in the future, the coating must be removed and this can cause additional problems. Sometimes the content of the surface coating is not known due to inadequate documentation. Therefore stabilising archaeological coins with the help of surface coatings does not generally serve its purpose because the process is not entirely reversible and also it does not ensure the coins' complete protection. In this case, the effect of intense light on coated and uncoated coins was examined in order to determine whether exhibition in display cases of museums affects the appearance of the coins.

Experiment: For the trial, some recently cleaned group B coins from the Livonian War period were selected, some of which were coated with microcrystalline wax (Renaissance, Picreator Ltd), some with Paraloid B-72 (15% solution in acetone) and some were left uncoated. Half of the surfaces of the coins was covered with a lightproof material and the coins were placed near a fluorescent lamp where the light intensity was 1600 lux. The trey with the coins was kept there for a whole year, during which coins were exposed to light approximately for a total of 3,000 hours.

Result: It appeared that the light alone influences the coins rather little, because distinguishing between the exposed and unexposed parts of the coins is visually impossible (**figure 28**). A barely noticeable difference was noted in some uncoated coins and in coins coated with wax.

Conclusion: Protecting coins' surface with coating is not necessary for coins appropriately cleaned because the effect of light to their surface is minimal and the protective effect of the coating is also doubtful. The need for coating may arise mainly with group B coins. Out of the coatings tried out, only Palaroid B-72 is worth considering. Since tarnishing of coins' surface is primarily caused not by light but by chemical compounds afloat in the air, coating must be able to insulate the surface from the outside environment. Besides Paraloid B-72 special lacquers, such as Incralac and Frigilene are also in the list of options. Stabilising coins' surface with insulating coating may also become necessary when they have previously been cleaned with a blaster or some other destructive method.

Conclusions

On the basis of the results of this work the following can be recommended for the conservation of Estonian coins of the early post-medieval period:

- There are three main types of chemical agents that can be recommended for cleaning debased silver coins: acidic, alkaline and complexing solutions. The effect of different types of reagents complements each other and they can be combined, if necessary.
- Ammonia solution should be avoided, for when reacting with copper it damages the structure of the surface layer of coins.
- The galvanic and electrolytic methods are unsuitable for cleaning of silver-copper alloys (which includes nearly all silver coins from early post-medieval period), because a layer of elemental copper may be reduced on the surface of the coins.
- Microblasting cannot be recommended for cleaning debased silver coins, for they damage the thin surface layer that is rich in silver. In exceptional cases, we might recommend using blaster with soft abrasive for coins containing more silver.
- Laser beam is not a very suitable means for cleaning coins, because it is not able to remove the thin layer of cuprite from the metal surface of debased silver coins.

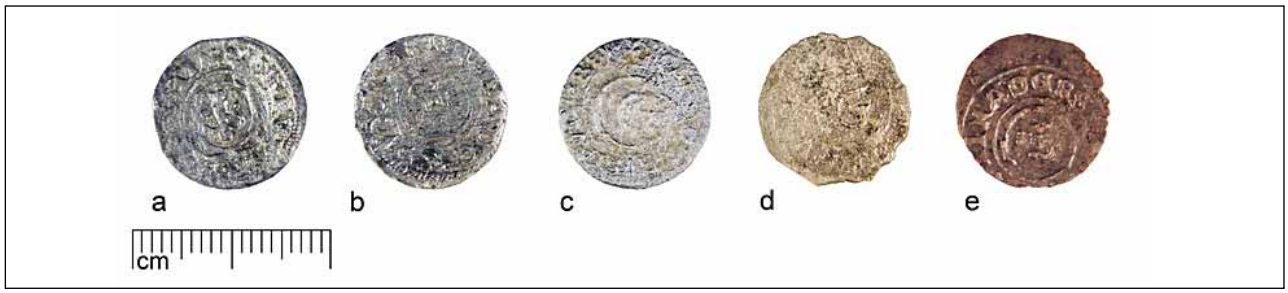

Fig. 27: Coins of group B from the same hoard after different treatment: a - SM 10663:1809, alkaline Rochelle solution; b - SM 10663:4, formic acid solution; c - SM 10663:1803, sodium tiosulphate solution; d - SM 10663:1805, electrolysis in sodium carbonate solution; e - SM 10663:1821, galvanic treatment in alkaline Rochelle solution.

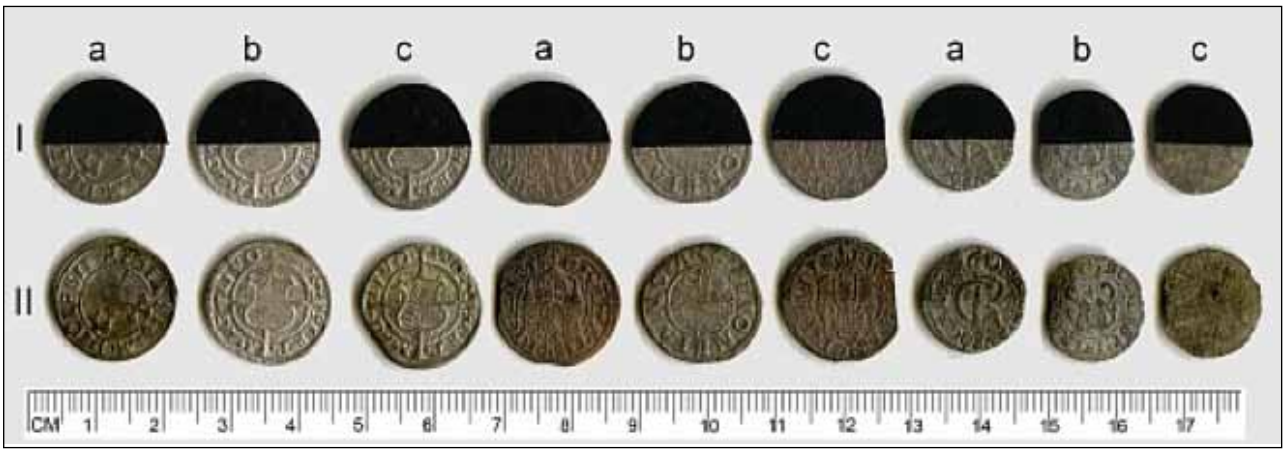

Fig. 28: The effect of light on coated and uncoated coins: **I** - before the experiment, **II** - after the experiment; **a** – uncovered, **b** – Paraloid B-72, 15% solution, **c** – microcrystalline wax.

Electrochemical treatment			
Type/agent	**Solution**	**Recommendations**	
Galvanic	sodium carbonate	effect questionable	
	alkaline Rochelle salt	not recommended	
Electrolytic	sodium carbonate	not recommended	
	sodium hydroxide	not recommended	
	formic acid	effect questionable	
Chemical treatment			
Acidic	acetic acid	recommended*	
	formic acid	recommended	
	EDTA	recommended	
Alkaline	alkaline Rochelle salt	recommended	
	ammonia	not recommended	
Complexing	sodium tiosulphate	recommended	
	thiourea	not recommended	
Reducing	alkaline dithionite	effect questionable	

Table 2: Recommendations for cleaning debased archaeological silver coins with electrochemical and chemical methods, based on current experiments. * All recommended solutions have their terms and limitations, for details see above.

Moreover, the laser impulse damages the surface of the coin by melting locally the surface layer of the coin.

- Stabilisation of properly cleaned and correctly preserved coins by coating is generally not necessary. Stabilising may appear necessary when the preservation environment contains chemicals damaging the metal of coins or if coins have been previously cleaned with a blaster or some other destructive method.

Recommendations about particular chemical agents are presented in Table 2, based on the results with the low-grade (group B) silver coins, as they are more sensitive.

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Notes

[1] Numbers in brackets refer to the names of the hoards and sample IDs.

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