Archaeometric analysis of Alesia group brooches from sites in Slovenia

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Izvleček

Z rentgensko fluorescenco (XRF), z metodo protonsko vzbujenih rentgenskih žarkov (PIXE) in z vrstično elektronsko mikroskopijo (SEM) smo analizirali 18 fibul skupine Alesia s slovenskih najdišč. Z XRF smo ugotovili približno sestavo zlitin. Za meritve s PIXE smo na vsaki fibuli izbrali eno do sedem merskih mest. Na mestih, s katerih smo odstranili korozijo do kovinskega jedra, smo merili osnovno zlitino; na drugih smo merili patinirano površino, s čimer smo skušali odkriti morebitne sledove pokositrenja, posrebritve in podobno. Vrstični elektronski mikroskop smo uporabili predvsem za ugotavljanje, kaj pomeni visok delež kositra na površini fibule št. 5.

Ugotovili smo, da je štirinajst fibul narejenih iz medenine, ena iz zlitine bakra s kositrom in cinkom, tri pa so bronaste. Analize so tudi pokazale, da so bile nekatere fibule (medeninaste in bronaste) pokositrene.

Ključne besede: fibule vrste Alesia, arheometrija, XRF, PIXE, SEM EDX

Abstract

The methods of X-ray fluorescence, proton-induced X-ray emission (PIXE) and scanning electron microscopy (SEM) were used for analysis of 18 brooches of the group Alesia from Slovenian sites. XRF served for an approximate determination of the alloy composition. For the analysis with PIXE, up to seven areas were selected on each brooch. Basic alloy was determined in the areas from which we removed the corrosion layer down to the metal core; in the other areas we measured the corroded surfaces with an aim to detect tinning, silvering or other type of plating. The scanning electron microscope was mainly used for explanation of a high percentage of tin at the surface of the brooch No.5.

It was found out that fourteen brooches were made of brass, one of gunmetal and three of bronze. The analysis showed further that some of the brooches (made of brass and bronze) were tinned.

Keywords: brooches of the group Alesia, archaeometry, XRF, PIXE, SEM EDX

1. INTRODUCTION

The study involved eighteen brooches of the Alesia group from Slovenian sites. Our main interest was to find out whether the brooches were made of bronze, brass or gunmetal (cf. Istenič 2005).

The presence or absence of zinc in the brooch alloys was determined by X-ray fluorescence analysis (XRF) applied to the unprepared (i.e. corroded) surface of the objects. For a more accurate determination of the artefact composition, the technique of proton-induced X-ray emission spectrometry (PIXE) was used. Small areas on the surface of the objects, from which we removed corrosion, were analysed. Other accurate analytical methods that were on our disposal (for example ICP AES) were not convenient for our purpose as the investigated objects were rather thin. However, the results obtained by the PIXE method were accurate enough for the purpose of our research.

Investigations by scanning electron microscope (SEM) and electron-induced X-ray spectroscopy (EDX) were necessary for the explanation of a rather high quantity of tin at the surface of brooch No. 5.

Istenič

2. X-RAY FLUORESCENCE SPECTROSCOPY (EDS XRF)

The analyses were carried out at the National Museum of Slovenia using a Model PEDUZO 01/Am/Sip-250 X-ray analyser that was produced at the Jožef Stefan Institute.[1] The measurements involved a circular area of 11 mm diameter and were limited to a thin surface layer of the object, reaching a depth of only a few ten micrometers.

The unprepared surface, i.e. the corrosion layer at the surface of the brooches was investigated. For this reason, the analytical results do not give the actual alloy composition, but allow an assumption about its approximate composition. As our main interest was to detect brass or gunmetal brooches, the presence or absence of zinc was of main importance. Due to solubility of zinc in the corrosion products we expected that the proportion of zinc in the corrosion layer would be significantly lower than in the metal core of the object.

Among the 18 investigated brooches, the presence of zinc was detected in fourteen brooches (Nos. 1-2, 4, 8-18). The measured content of zinc varied between 5 and 17%.[2] No zinc was found in the brooches Nos. 3, 5, 6 and 7.

Milić, Istenič

3. PROTON-INDUCED X-RAY EMISSION SPECTROSCOPY (PIXE)

3.1 Description of the method

The measurements were made at the Tandetron Accelerator of the Jožef Stefan Institute, using a measuring line with the proton beam in air. The protons were accelerated up to the energy of 2.5 MeV, but passing an 8 μm thick aluminium foil and a 1 cm thick air gap, they lost some energy so the impact energy at the target was about 2.2 MeV. The target was oriented with the normal to the surface at an angle of 22.5^0 to the proton beam. The same angle was used between the surface normal and the direction towards the X-ray detector. A scintillator made from ruby powder on scotch-tape monitored the area where the proton beam hit the target. Aiming of the beam was hindered by parallax, so measurements on the same area were repeated several times. We inferred from the results in which the beam hit the prepared area most accurately.

Detection of induced X-rays was performed by a Si(Li) detector with an energy resolution of 160 eV at 5.9 keV. During the measurement, the detector was equipped with an aluminium absorber of 0.3 mm thickness. With such a thick absorber we improved the relative sensitivity for hard X-rays around tin, so the minimum detection limit in this region was 0.1%. The thick absorber also improved discrimination between the K X-ray lines of arsenic and the L X-ray lines of lead, as the absorber increased the relative intensity of arsenic K_β lines and lead L_β lines in the spectra. The minimum detection limit for arsenic was 0.03%. A drawback of the thick absorber was partial overlapping of the iron K X-ray lines with the escape peaks of copper, so the absolute uncertainty in determination of iron was about 0.5%. The absorber also removed the X-ray lines with energies smaller than 5 keV, that is the L X-ray lines of tin and the K X-ray lines of light elements.

The presence of zinc in the spectra was determined according to the K_β zinc line. When treating the spectra with the AXIL program, the asymmetric copper K_β line gave a small apparent intensity of the zinc K_α line even if no zinc were present. In pure copper we would thus determine a virtual concentration of zinc of about 0.4%. As a criterion for the presence of zinc in the sample we then relied on the subjective identification of the zinc K_β line. It was thus reasonable to set the detection limit for zinc at about 1%.

The measured X-ray intensities were transformed into concentrations (in weight %) by the method of independent parameters (see Šmit et al. 2005), i.e. using known X-ray production cross sections, proton stopping force and X-ray attenuation coefficients, as given in the relevant literature. Among the secondary effects on X-ray production we considered fluorescence induced by other, harder X-rays in the target. For normalization we took into account that the sum of all weight fractions in the

[1] The radiation source was Am-241 with an activity of 25 mCi. The X-ray detector was a Si PIN diode with a resolution of 250 eV at 5.9 keV. The spectrum was analyzed in a 1024-channel MCA with a differential nonlinearity smaller than 2% and integral nonlinearity smaller than 1%. The sensitive part of the diode is kept in vacuum and is equipped with a Be window of 25 micrometer thickness. The PIN diode and preamplifier FET are Peltier-cooled down to 235 K. The adjustment of the system was preset during manufacture, so the spectral region extends between 3 and 30 keV with a dispersion of about 30 eV/channel.

[2] No. 1 (17%), 2 (6%), 4 (4.6%), 8 (5%), 9 (5.6%), 10 (9.8%), 11 (10%), 12 (4%), 13 (5.4%), 14 (12.3%), 15 (6%), 16 (11.2%), 17 (6.2%), 18 (9.3%).

target equals unity, and thus avoided calibration of the detector solid angle and measurements of the proton number during each run. Measurement of the brass standard 1107 containing 1.04% tin was used to monitor the accuracy of the method. The concentrations of the standard were reproduced with an accuracy of a few percent, so the uncertainty of the method can be safely put at ±5%. For the elements around tin, this value should be increased by the statistical uncertainty, which was about 10% for low tin concentrations (~0.3%).

In addition to the areas from which corrosion was removed, we also measured the unprepared surfaces of the brooches in order to identify surface treatments such as silvering and tinning. As the method of PIXE is not sensitive to light elements (oxygen, carbon, hydrogen), we assumed that the metals were bound in chemical compounds which together sum to 100%. Copper was assumed to be bound in malachite $CuCO_3.Cu(OH)_2$, and the other metals in oxide form. A typical percentage of metals in such a corrosion layer varied around 60%. We also made calculations of the relative elemental concentrations in the metallic component, normalizing the sum of metal concentrations to 100%. The values determined in this way differed only slightly from the values calculated for an initial assumption of a pure metal target.

3.2 **Description of measurements, results and commentary**

The PIXE method was used for the analysis of two types of areas: 1) prepared areas of 2-3 mm^2, from which the corrosion layer was removed down to the metal core, and 2) unprepared areas, i.e. the corroded surface of the brooches, where we tried to detect possible traces of surface treatment (as silvering, tinning, cf. Šmit 2003; Istenič, Milić, Šmit 2003, 291-292). The results of measurements of unprepared surfaces are given in the tables below in two ways: 1) metal concentrations, calculated as constituent parts of carbonates and oxides (labelled in the tables as 'calc. for comp.'), and 2) relative proportions of metal elements that we obtained by normalizing the metal content in compounds to 100% (labelled as 'norm. metals').

The results of the measurements of prepared areas (the surface corrosion and a thin metal layer were removed) gave information about the composition of the metal core of the brooches. Checking the prepared areas under a binocular microscope or magnifying hand lens showed that complete removal of corrosion from the surface area was rather difficult. The metal core of a few brooches was in such bad condition that it did not allow the corrosion layer to be thoroughly removed from the surface. The reliability of analysis therefore depends on the efficiency of the removal of the corrosion and on the precision of aiming of the proton beam on the prepared area. For these reasons, the measurements were repeated several times, usually after additional cleaning and/or increase of the measuring area. Very small areas were measured by a narrow beam (0.3 mm) in addition to the measurement by a normal beam (of 2 mm diameter). The values given in the tables were obtained by a normal beam, unless stated differently (see "Notes"). Only the results of selected measurements are given, usually the measurements after the first and after the last cleaning of the area, or the measurements where the beam optimally hit the target (prepared area). In a few cases (see No. 4, area 1) we give more measurements for documentary purposes. After additional cleaning (i.e. corrosion removal), the content of zinc was usually higher (see No. 1, areas 1 and 2 etc.).

A large part of the iron (together with some tin and lead) measured on the prepared areas very likely originates from the remnants of corrosion, or from corrosion on the surrounding, unprepared surface, if aiming of the proton beam was inaccurate. The content of iron is reliable up to an absolute uncertainty of 0.5%. Iron was measured more accurately with a narrow beam (diameter 0.3 mm), as the absorber in this case was only a kapton foil 100 μm thick. The concentrations of iron from these measurements are therefore given with two decimal digits.

Very small concentrations of zinc in the corrosion layer at the surface of the brooches (see No. 2, area 3 etc.) clearly demonstrate dezincification, i.e. non-durability of this element at the surface. Dezincification can also be observed when comparing the measurement results of the prepared and unprepared areas (see No. 2, areas 1 and 3, No. 3, areas 1 and 3, etc.).

On the surface of the brooch No. 12 the concentration profile of zinc was measured by the differential PIXE method (Šmit, Holc, 2004). In this technique, a series of measurements is made in the same spot at different proton energies, thus reaching deeper and deeper regions of the target. The maximum thickness of the concentration profile depends on the range of protons at the highest energy and is usually below 10 μm. The measured surface of this brooch was covered by a very thin corrosion layer which did not form on the primary surface of the brooch (cf. Istenič 2005, No. 12).

As shown in *Fig. 1,* the concentration of zinc is about 1% for the first 6 µm below surface, with a tendency to increase with depth.

The results of measurements are given in the following tables. Only the elements that exceeded the detection limit in the spectra are indicated.

Table 1: No. 1. Narodni muzej Slovenije, Inv. No. R 17393; *Pl. 1:* 1.
Tab. 1: Št. 1. Narodni muzej Slovenije, inv. št. R 17393; *t. 1:* 1.

Area / Mesto meritve	Description / Opis	Notes / Opombe	Fe	Cu	Zn	As	Pb	Ag	Sn
1	metal core, 1st removal of corrosion / jedro, 1. odstr. korozije		1.2	79.1	19.0	0.05	0.22	0.1	0.4
=	metal core, 2nd removal of corrosion / jedro, 2. odstr. korozije		1.2	78.2	19.9		0.36		0.4
2	metal core, 1st removal of corrosion / jedro, 1. odstr. korozije			81.6	17.6		0.19	0.1	0.5
=	metal core, 2nd removal of corrosion / jedro, 2. odstr. korozije		1.1	78.4	19.8		0.31	0.1	0.4
3	corrosion / korozija	calc. for comp. / rač. za spojine	0.8	49.0	10.8	0.01	0.04	0.1	0.3
=	=	norm. metals / norm. kovine	1.3	80.3	17.7	0.02	0.07	0.1	0.5
4	corrosion / korozija	calc. for comp. / rač. za spojine	0.8	49.4	10.2	0.02	0.05	0.1	0.3
=	=	norm. metals / norm. kovine	1.3	81.2	16.8	0.03	0.08	0.1	0.5

Commentary:

The corrosion was removed from areas 1 and 2; the respective surface shows a yellow metallic shine. Areas 3 and 4 consisted of areas on the unprepared surface on the underside of the bow of the brooch.

The results of the measurements in areas 1 and 2 indicate that the brooch was made of brass containing at least c. 20% zinc. The measurements in areas 3 and 4 differ only little from the results in areas 1 and 2, which confirms that the dark-brown corrosion layer was not formed on the primary surface, but after the primary corrosion layer was removed (cf. Istenič 2005, No. 1). This corrosion was very likely formed by treating the brooch with potassium polysulfide, which was not detected during measurements as we did not measure elements lighter than iron.

Table 2: No. 2. Narodni muzej Slovenije, Inv. No. P 19282; *Pl. 1:* 2.
Tab. 2: Št. 2. Narodni muzej Slovenije, inv. št. P 19282; *t. 1:* 2.

Area / Mesto meritve	Description / Opis	Notes / Opombe	Fe	Ni	Cu	Zn	As	Pb	Ag	Sn
1	metal core, 1st removal of corrosion / jedro, 1. odstr. korozije		3.4		76.6	15.6	0.05	1.5	0.2	2.6
=	metal core, 2nd removal of corrosion / jedro, 2. odstr. korozije		1.0	0.15	76.4	21.3		0.49		0.6
2	metal core, 1st removal of corrosion / jedro, 1. odstr. korozije		2.3		79.2	15.2	0.04	0.98	0.2	2.0
=	metal core, 2nd removal of corrosion / jedro, 2. odstr. korozije		1.7	0.1	76.0	21.0		0.53		0.8
3	corrosion / korozija	calc. for comp. / rač. za spojine	1.2		54.7	0.9		0.28	0.1	1.3
=	=	norm. metals / norm. kovine	2.1		93.5	1.5		0.48	0.2	2.2

Commentary:

A great majority of corrosion was removed from areas 1 and 2; the respective surface shows a brown-yellow metallic shine. Area 3 represents corrosion on the primary surface of the brooch, on the upper side of the bow.

The results of the measurements indicate that the brooch was made of brass containing at least c. 21% zinc. The surface was not plated by any other metal.

Table 3: No. 3. Goriški muzej Nova Gorica, Inv. No. 7; *Pl. 1:* 3.
Tab. 3: Št. 3. Goriški muzej Nova Gorica, inv. št. 7; *t. 1:* 3.

Area / Mesto meritve	Description / Opis	Notes / Opombe	Fe	Cu	Zn	As	Pb	Ag	Sn
1	metal core / jedro		0.3	90.0	3.1	0.09	1.1		5.4
=	=	repeated measurement / ponovitev mer.	0.8	88.1	3.1	0.15	1.2		6.8
2	corrosion / korozija	calc. for comp. / rač. za spojine	1.5	52.3	0.7		0.6	0.4	3.9
=	=	norm. metals / norm. kovine	2.6	88.0	1.2		1.0	0.7	6.5

Commentary:
A great majority of the corrosion layer was removed from area 1; the respective surface shows a brown-yellow metallic shine. The area was measured with a normal beam as well as with a narrow one. The corrosion on the surface of the brooch was measured in the area 2.

The results of the measurements indicate that the brooch was made of gunmetal, i.e. an alloy of copper (c. 90%), tin (c. 6%) and zinc (c. 3%). The alloy also contains about 1% of lead. This alloy could be the result of melting together bronze and scrap brass. The surface was not plated by any other metal.

Table 4: No. 4. Narodni muzej Slovenije, Inv. No. R 17281; *Pl. 1:* 4.
Tab. 4: Št. 4. Narodni muzej Slovenije, inv. št. R 17281; *t. 1:* 4.

Area / Mesto meritve	Description / Opis	Notes / Opombe	Fe	Cu	Zn	Pb	Ag	Sn
1	metal core, 1st removal of corrosion / jedro, 1. odstr. korozije		1.6	82.0	14.6	0.31	0.1	1.4
=	metal core, 2nd removal of corrosion / jedro, 2. odstr. korozije		1.2	80.5	16.9	0.25		1.2
=	metal core, 3rd removal of corrosion / jedro, 3. odstr. korozije		1.4	81.5	15.5	0.27	0.06	1.2
=	=	repeated measurement / ponovitev mer.	1.2	81.0	16.4	0.29		1.1
=	=	repeated measurement / ponovitev mer.	0.9	81.9	15.5	0.29		1.3
=	=	repeated measurement / ponovitev mer.	1.1	80.7	16.8	0.26		1.2
2	metal core, 1st removal of corrosion / jedro, 1. odstr. korozije		1.8	83.7	12.3	0.43	0.1	1.7
=	metal core, 2nd removal of corrosion / jedro, 2. odstr. korozije		1.2	81.4	15.9	0.30		1.2
3	corrosion / korozija	calc. for comp. / rač. za spojine	5.9	45.5	3.9	1.3	0.3	6.6
=	=	norm. metals / norm. kovine	9.3	71.6	6.1	2.1	0.5	10.4
4	=	calc. for comp. / rač. za spojine	6.6	44.1	3.6	1.3	0.3	8.4
=	=	norm. metals / norm. kovine	10.3	68.6	5.6	2.0	0.5	13.1

Commentary:
The great majority of corrosion was removed from areas 1 and 2; the respective surface shows a yellow metallic shine. Both areas were measured several times. The areas 3 and 4 are located on the unprepared surface on the lower and upper side of the bow, respectively.

The results of the measurements indicate that the brooch was made of brass containing at least c. 17% zinc. The relatively large content of iron and tin very likely originate from the remnants of corrosion in areas 1 and 2. The measurements of areas 3 and 4 do not suggest that the surface was plated with another metal.

Table 5: No. 5. Narodni muzej Slovenije, Inv. No. R 19080; *Pl. 1:* 5.
Tab. 5: Št. 5. Narodni muzej Slovenije, inv. št. R 19080; *t. 1:* 5.

Area / Mesto meritve	Description / Opis	Notes / Opombe	Fe	Cu	As	Pb	Sn
1	corrosion / korozija	calc. for comp. / rač. za spojine		23.1	0.2	0.5	46.6
=	=	norm. metals / norm. kovine		32.8	0.2	0.7	66.3
2	metal core, 1st removal of corrosion / jedro, 1. odstr. korozije			56.3	0.2	0.3	43.1
=	metal core, 2nd removal of corrosion / jedro, 2. odstr. korozije		1.3	80.7	0.1	0.08	17.8
3	metal core, 1st removal of corrosion / jedro, 1. odstr. korozije			78.5	0.1	0.16	21.3
=	metal core, 2nd removal of corrosion / jedro, 2. odstr. korozije		1.4	83.0	0.07	0.17	15.4
4	metal core / jedro		1.5	84.8	0.1	0.08	13.5
5	corrosion / korozija	calc. for comp. / rač. za spojine	1.3	43.7	0.06	0.11	17.8
=	=	norm. metals / norm. kovine	2.1	69.4	0.1	0.17	28.3

Commentary:

The great majority of corrosion was removed from the areas 2, 3 and 4; the respective surfaces show brown-reddish metallic shine. The areas 2 and 3 were relatively small and were measured several times. Area 1 was chosen on the corrosion layer that formed on the primary surface, whereas the area 5 represents corrosion that formed after the primary corrosion on the original surface had peeled off.

The measurements indicate that the brooch was made of bronze. As the fraction of tin in area 1 is rather large, and repeated measurements on the areas 2 and 3 indicated that the percentage of tin decreases after each subsequent preparation of the area, the estimated content of tin in the metal core is below 13%.

A large amount of tin measured in the corrosion layer formed on the primary surface (area 1) might be result of tinning or of corrosion processes (cf. Meeks 1993). An investigation by scanning electron microscope showed that the brooch was probably not tinned (see below).

Table 6: No. 6. Narodni muzej Slovenije, Inv. No. P 19283; *Pl. 1:* 6.
Tab. 6: Št. 6. Narodni muzej Slovenije, inv. št. P 19283; *t. 1:* 6.

Area / Mesto meritve	Description / Opis	Notes / Opombe	Fe	Ni	Cu	Zn	As	Pb	Ag	Sn
1	metal core / jedro		0.8		81.9	1.5	0.22	2.8		12.8
=	metal core / jedro	narrow beam / ozek žarek	0.28	0.15	89.1			2.5		8.00
2	metal core, 1st removal of corrosion / jedro, 1. odstr. korozije	=			89.4	1.0	0.06	2.2	0.1	7.2
=	metal core, 2nd removal of corrosion / jedro, 2. odstr. korozije		0.9	0.25	88.5	1.0		2.6	0.1	6.7
3	corrosion / korozija	calc. for comp. / rač. za spojine	2.3		26.4	0.8	0.45	4.1		35.2
=	=	norm. metals / norm. kovine	3.3		38.1	1.2	0.6	5.9		50.8

Commentary:

The great majority of corrosion was removed from the areas 1 and 2; the respective surfaces show a brown-reddish metallic shine. The point 1 is small; therefore it was measured also with a narrow beam. The area 2 was relatively large after the second removal of corrosion, but it still contained small pits filled with corrosion products. The area 3 represents corrosion formed at the primary surface on the upper part of the brooch bow.

The results of measurements on area 2 indicate that the brooch was made of a copper alloy containing c. 7% tin, c. 2-3% lead and c. 1% zinc. A small, but certain fraction of zinc presumably originated from the use of scrap brass.

The lack of a shiny silvery surface indicates that the brooch was probably not tinned.

Table 7: No. 7. Narodni muzej Slovenije, Inv. No. R 1464; *Pl. 1:* 7.
Tab. 7: Št. 7. Narodni muzej Slovenije, inv. št. R 1464; *t. 1:* 7.

Area / Mesto meritve	Description / Opis	Notes / Opombe	Fe	Ni	Cu	Zn	As	Pb	Ag	Sn
1	"silvery" surface / "srebrna" površina		2.5		26.3			12.1		30.5
2	= , poorly preserved / = , slabo ohr.		4.9		39.4			9.2	0.2	13.0
3	metal core, 1st removal of corrosion / jedro, 1. odstr. korozije		1.0	0.2	86.4	0.4	0.25	4.3		7.4
=		narrow beam / ozek žarek	0.36	0.1	83.7			5.6		10.2
=	metal core, 2nd removal of corrosion / jedro, 2. odstr. korozije				88.2		0.20	4.8	0.06	6.8
=		repeated measurement / ponovitev mer.	0.9	0.2	86.8		0.19	4.8	0.1	7.0
4	corrosion / korozija	calc. for comp. / rač. za spojine	2.9		38.5			7.1		17.7
=	=	norm. metals / norm. kovine	4.4		58.2			10.7		26.7
5	metal core / jedro		1.4	0.2	82.2		0.32	6.2		9.6

Commentary:

The smooth silvery layer on the surface of the upper side of the brooch was measured in area 1 where it is relatively well preserved, and in the area 2 where its preservation was less good. The great majority of corrosion was removed from the areas 3 and 5, so a brown-reddish shiny metallic core became visible. Area 3 was measured several times. Area 4 was selected on the unprepared corroded surface on the underside of the brooch.

The results of measurements indicate that the brooch was made of bronze, containing c. 7% tin and c. 5% lead. The 0.4% concentration of zinc obtained in the first measurement of area 3 is close to the extreme detection limit; it was not repeated during the second measurement of the area on the better cleaned surface. The presence of zinc in the metal core is therefore below the detection limit.

The thin silvery layer on the upper surface of the brooch bow most probably represents tinning.

Table 8: No. 8. Narodni muzej Slovenije, Inv. No. R 18974; *Pl. 1:* 8.
Tab. 8: Št. 8. Narodni muzej Slovenije, inv. št. R 18974; *t. 1:* 8.

Area / Mesto meritve	Description / Opis	Notes / Opombe	Fe	Cu	Zn	As	Pb	Ag	Sn
1	metal core, 1st removal of corrosion / jedro, 1. odstr. korozije		2.1	81.6	13.0		1.56	0.2	1.5
1	metal core, 2nd removal of corrosion / jedro, 2. odstr. korozije		1.3	80.9	16.2		0.91		0.8
1	=	narrow beam / ozek žarek	0.25	80.7	18.6		0.45		
1	metal core, 3rd removal of corrosion / jedro, 3. odstr. korozije		0.5	77.9	20.1		0.98		0.6
1	=	repeated measurement / ponovitev mer.	0.8	77.8	19.6		1.1		0.7
2	metal core, 1st removal of corrosion / jedro, 1. odstr. korozije		2.1	84.3	10.7	0.05	0.95	0.2	1.7
2	metal core, 2nd removal of corrosion / jedro, 2. odstr. korozije		1.8	81.7	15.0		0.78		0.7
2	=	narrow beam / ozek žarek	0.26	80.8	18.1		0.92		

3	corrosion / korozija	calc. for comp. / rač. za spojine	2.4	51.1	2.7	0.05	1.5	0.1	1.9
3	=	norm. metals / norm. kovine	4.0	85.4	4.6	0.1	2.5	0.2	3.2
4	=	calc. for comp. / rač. za spojine	2.4	52.0	2.6		1.7		1.7
4	=	norm. metals / norm. kovine	4.0	86.0	4.3		2.9		2.8

Commentary:

On the areas 1 and 2, selected on the underside of the bow, the corrosion was removed down to a shiny yellow metal core. Area 1 was significantly larger and more thoroughly cleaned of corrosion. The measurements were performed several times, including those with the narrow beam. On areas 3 and 4, situated on the unprepared surface of the upper side of the bow, the corrosion formed on the primary brooch surface was measured.

The results of the measurements indicate that the brooch was made of brass containing at least c. 20% zinc. There was no surface plating.

Table 9: No. 9. Goriški muzej Nova Gorica, Inv. No. 10; *Pl. 1:* 9.
Tab. 9: Št. 9. Goriški muzej Nova Gorica, inv. št. 10; *t. 1:* 9.

Area / Mesto meritve	Description / Opis	Notes / Opombe	Fe	Cu	Zn	Pb	Ag	Sn
1	metal core / jedro		1.6	79.2	15.4	0.86	0.1	2.8
2	corrosion / korozija	calc. for comp. / rač. za spojine	5.5	46.4	1.7	0.6	0.2	6.7
=	=	norm. metals / norm. kovine	9.0	75.9	2.8	1.0	0.4	11.0

Commentary:

On area 1 selected on the lower side of the brooch bow, the great majority of corrosion was removed down to the yellow, shiny metal core. Area 2 was selected on the unprepared surface representing corrosion products, formed on the primary surface of the brooch.

The results of the measurements indicate that the brooch was made of brass containing at least c. 15% zinc. The fraction of zinc was presumably larger. Namely, the relatively high contents of iron and tin suggest that there were remnants of corrosion on the prepared area, or that the proton beam also hit the corrosion around area 1. The surface of the brooch had no surface coating.

Table 10: No. 10. Narodni muzej Slovenije, Inv. No. R 17319; *Pl. 1:* 10.
Tab. 10: Št. 10. Narodni muzej Slovenije, inv. št. R 17319; *t. 1:* 10.

Area / Mesto meritve	Description / Opis	Notes / Opombe	Fe	Ni	Cu	Zn	As	Pb	Bi	Ag	Sn
1	metal core, 1st removal of corrosion / jedro, 1. odstr. korozije		1.7		80.0	17.5		0.27			0.6
1	metal core, 2nd removal of corrosion / jedro, 2. odstr. korozije			0.10	79.2	19.9	0.01	0.28			0.5
2	metal core, 1st removal of corrosion / jedro, 1. odstr. korozije		0.9		80.6	17.7		0.26		0.06	0.5
2	metal core, 2nd removal of corrosion / jedro, 2. odstr. korozije		1.3	0.06	79.0	18.8		0.26	0.09		0.5
3	corrosion/ korozija	calc. for comp. / rač. za spojine	3.0		48.9	2.2		4.8		0.3	2.9
=	=	norm. metals / norm. kovine	4.8		78.7	3.5		7.8		0.5	4.7
4	corrosion / korozija	calc. for comp. / rač. za spojine	1.8		53.6	1.4		1.4		0.1	1.2
	=	norm. metals / norm. kovine	3.0		90.1	2.4		2.4		0.1	2.0

Commentary:

On the areas 1 and 2 (selected on the underside of the brooch bow), the corrosion layer was removed down to the yellow, shiny metal core; both areas were measured several times. Area 1 was larger and more thoroughly cleaned. Areas 3 (at the underside of the brooch bow) and 4 (at the upper side of the bow) represent the unprepared surface - area 4 the corrosion that might have been formed on a badly preserved primary surface.

The results of measurements indicate that the brooch was made of brass containing at least c. 20% zinc. The surface exhibited no traces of metal plating.

Table 11: No. 11. Narodni muzej Slovenije, Inv. No. Zn198/49; *Pl. 1:* 11.
Tab. 11: Št. 11. Narodni muzej Slovenije, inv. št. Zn198/49; *t. 1:* 11.

Area / Mesto meritve	Description / Opis	Notes / Opombe	Fe	Ni	Cu	Zn	As	Pb	Ag	Sn
1	"silvery" surface, not well preserved / "srebrna" površina, slabše ohr.		4.8		78.6	7.2		0.79	0.4	8.1
2	"silvery" surface, well preserved / "srebrna" površina, dobro ohr.		2.1		72.3	8.9		0.52		16.2
3	metal core / jedro		0.6		79.6	19.1		0.16		0.6
4	hinge axis / os tečaja		92.2		6.6	1.2				
5	metal core, 1st removal of corrosion / jedro, 1. odstr. korozije		1.4		79.4	18.0		0.30	0.1	0.8
=	metal core, 2nd removal of corrosion / jedro, 2. odstr. korozije		1.4		77.1	20.6		0.33		0.7
6	metal core, 1st removal of corrosion / jedro, 1. odstr. korozije		1.5		79.0	18.4		0.35		0.7
=	metal core, 2nd removal of corrosion / jedro, 2. odstr. korozije		0.7	0.10	76.9	21.2		0.42	0.09	0.6
7	corrosion / korozija	calc. for comp. / rač. za spojine	6.3		50.1	2.2	0.02	0.56	0.2	2.3
=	=	norm. metals / norm. kovine	10.2		81.2	3.6	0.03	0.91	0.3	3.7

Commentary:

Areas 1 and 2 were selected on the shiny silvery layer on the upper side of the brooch bow, showing different states of preservation. On areas 3 (on the leg), 5 and 6 (on the underside of the brooch), the corrosion layer was removed down to the shiny yellow metal core. Area 4 lies at the edge of the iron pin of the hinge. Area 7 was chosen on the underside of the brooch bow, on the corrosion layer that was very likely formed on the primary surface of the brooch.

The results of the measurements indicate that the brooch was made of brass, containing at least about 21% zinc. The high percentage of tin on areas 1 and 2 indicates that the silvery and shiny coating at the upper surface of the brooch is tinned. Namely, there is less than 1% of tin in the basic alloy. (Compare also chapter 4.)

Table 12: No. 12. Narodni muzej Slovenije, Inv. No. R 19078; *Pl. 1:* 12.
Tab. 12: Št. 12. Narodni muzej Slovenije, inv. št. R 19078; *t. 1:* 12.

Area / Mesto meritve	Description / Opis	Notes / Opombe	Fe	Cu	Zn	As	Pb	Ag	Sn
1	metal core / jedro		1.2	81.1	16.6		0.26	0.1	0.7
2	metal core / jedro		1.6	80.3	17.1		0.33	0.05	0.5
3	metal core, 1st removal of corrosion / jedro, 1. odstr. korozije		1.5	80.5	16.8		0.41		0.8
3	metal core, 2nd removal of corrosion / jedro, 2. odstr. korozije		0.6	78.1	20.4		0.39		0.6
4	"silvery" sheath / "srebrna" folija			5.5	0.3	0.2	4.9	79.1	9.9
5	corrosion around the hinge axis / korozija ob osi	calc. for comp. / rač. za spojine	53.3	12.4	0.6		0.7		0.5
5	=	norm. metals / norm. kovine	79.0	18.4	0.9		1.0		0.7

6	soldering / spajkanje			6.7	0.9	0.09	24.4		68.0
7	corrosion / korozija	calc. for comp. / rač. za spojine	0.7	54.4	1.46		0.36	0.2	1.6
=	=	norm. metals / norm. kovine	1.1	92.7	2.49		0.61	0.3	2.8

Commentary:

On areas 1, 2 and 3 (selected on the underside of the brooch), a great majority of the corrosion was removed so that the shiny yellow metal core was exposed. Area 3 was the largest and most thoroughly cleaned. Area 4 lies at the remains of a thin shiny silvery metal layer, and area 6 is positioned on a markedly rugged surface (presumably on the remains of soldering), both on the oval part of the upper side of the brooch. Area 5 was selected on the layer of corroded iron that covered part of the hinge.

Among the results of the measurements on the areas 1-3, those of area 3 are the most reliable. The brooch is then made of brass, containing at least about 20% zinc. The thin, shiny silvery layer (area 4) is silver, which was soldered on the substrate by an alloy of lead and tin (area 6; compare Nos. 13 and 14).

Table 13: No. 13. Narodni muzej Slovenije, Inv. No. P 19946; *Pl. 1:* 13.
Tab. 13: Št. 13. Narodni muzej Slovenije, inv. št. P 19946; *t. 1:* 13.

Area / Mesto meritve	Description / Opis	Notes / Opombe	Fe	Ni	Cu	Zn	Pb	Bi	Ag	Sn
1	metal core, 1st removal of corrosion / jedro, 1. odstr. korozije		1.3		84.5	13.4	0.28		0.1	0.4
1	metal core, 2nd removal of corrosion / jedro, 2. odstr. korozije		1.7	0.10	81.2	16.4	0.24	0.06		0.3
1	metal core, 3rd removal of corrosion / jedro, 3. odstr. korozije				81.5	17.9	0.34			0.3
1	=	repeated measurement / ponovitev mer.			81.5	17.8	0.31			0.5
3	smooth "silvery" area, corrosion removed / gladka "srebrna" površina, korozija odstranjena		1.2		51.6	1.6	0.39		3.5	41.7
3	=	repeated measurement / ponovitev mer.	0.8	0.06	50.0	1.8	0.61		4.8	41.9
4	remains of soldering / ostanki spajkanja	calc. for comp. / rač. za spojine	2.9		46.2	2.3	3.0		1.0	6.6
		norm. metals / norm. kovine	4.7		74.5	3.7	4.8		1.6	10.6
5	remains of "silvery" sheath with soldering beneath it / ostanki "srebrne" folije na spajkanju	calc. for comp. / rač. za spojine	1.9		5.83	1.25	11.2		7.4	58.3
5	=	norm. metals / norm. kovine	2.2		6.79	1.46	13.0		8.6	67.9
6	corrosion / korozija	calc. for comp. / rač. za spojine	2.5	0.07	51.4	3.2	0.95		0.1	1.5
6	=	norm. metals / norm. kovine	4.2	0.1	86.1	5.4	1.6		0.1	2.5
7	remains of "silvery" sheath with soldering beneath it / ostanki "srebrne" folije na spajkanju	calc. for comp. / rač. za spojine	0.7		2.90	2.02	9.2		13.1	53.9
7	=	norm. metals / norm. kovine	0.8		3.54	2.47	11.3		16.0	65.9

Commentary:

On area 1 (on the underside of the brooch bow), the great majority of corrosion was removed down to the shiny yellow metal core. Three areas were selected on the upper side of the oval broadening of the brooch (*Fig. 1*): areas 5 and 7 on the topmost "wrinkled" layer, area 4 on the lower surface that might represent remnants of soldering, and area 3 on the smooth surface at the lowest level which seems to lie below the soldering; on this area a thin layer of corrosion was removed, so it attained a silvery shine.

The results of the last two measurements in area 1 indicate that the brooch was made of brass containing at least about 18% zinc. The measurements of areas 4, 5 and 7 suggest that a silver foil was soldered on the oval broadening of the brooch bow (compare Nos. 12 and 14).

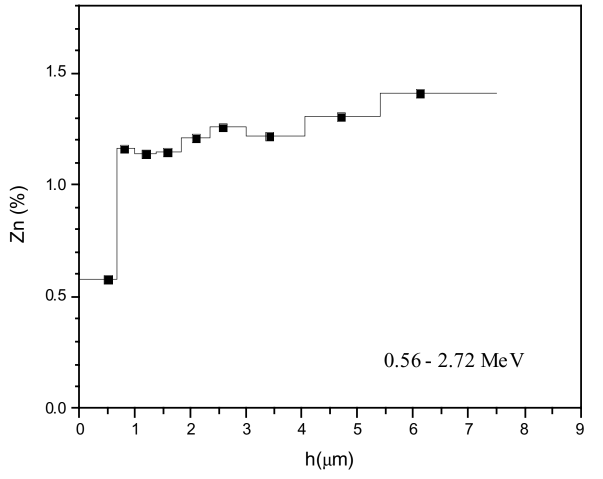

Fig. 1: Concentration profile of zinc in the near-surface region of brooch No. 12, measured by the differential PIXE method. The proton energy was varied between 0.56 and 2.72 MeV.
Sl. 1: Koncentracijski profil cinka v površinski plasti fibule kat. št. 12, izmerjen z diferencialno metodo PIXE. Energijo protonov smo spreminjali od 0,56 do 2,72 MeV.

Table. 14: No. 14. Zavod za varstvo kulturne dediščine, Območna enota Nova Gorica, Ident. No. 1874; *Pl. 1:* 14.
Tab. 14: Št. 14. Zavod za varstvo kulturne dediščine, Območna enota Nova Gorica, ident. št. 1874; *t. 1:* 14.

Area / Mesto meritve	Description / Opis	Notes / Opombe	Fe	Cu	Zn	Pb	Ag	Sn
1	metal core / jedro		1.2	79.9	18.1	0.21	0.06	0.5
1	metal core / jedro	narrow beam / ozek žarek	0.17	78.1	21.7			
2	corrosion / korozija	calc. for comp. / rač. za spojine	7.0	44.9	5.0	3.8	0.1	1.2
	=	norm. metals / norm. kovine	11.3	72.4	8.1	6.1	0.2	1.9
3	remains of soldering / ostanki spajkanja	calc. for comp. / rač. za spojine		6.21	2.33	15.1		55.2
	=	norm. metals / norm. kovine		7.89	2.96	19.1		70.0

Commentary:

The great majority of corrosion was removed from area 1 (small, selected on the leg) so that a yellow surface with a metal shine was exposed. The unprepared surface was measured on area 2. Area 3 was selected on the upper side of the oval broadening, where the surface is markedly rough and presumably represents remnants of soldering.

According to the results of the measurements in area 1, the brooch is made of brass (it contains at least 21% zinc). For soldering on the oval part of the bow (area 3), an alloy of tin and lead was used (compare Nos. 12 and 13).

Table 15: No. 15. Narodni muzej Slovenije, Inv. No. P 12982; *Pl. 1:* 15.
Tab. 15: Št. 15. Narodni muzej Slovenije, inv. št. P 12982; *t. 1:* 15.

Area / Mesto meritve	Description / Opis	Notes / Opombe	Fe	Cu	Zn	As	Pb	Ag	Sn
1	metal core, 1st removal of corrosion / jedro, 1. odstr. korozije		1.5	82.8	14.2	0.12	0.23		1.1
=	metal core, 2nd removal of corrosion / jedro, 2. odstr. korozije		0.7	81.2	17.0	0.07	0.26		0.7
3	corrosion / korozija	calc. for comp. / rač. za spojine	2.5	45.8	2.9	0.19	0.37	0.2	9.7
=	=	norm. metals / norm. kovine	4.1	74.3	4.7	0.3	0.6	0.3	15.7
4	=	calc. for comp. / rač. za spojine	2.9	50.6	2.6	0.15	0.16	0.1	3.3
=	=	norm. metals / norm. kovine	4.8	84.6	4.3	0.25	0.25	0.3	5.5

Commentary:

The great majority of corrosion was removed from areas 1 and 2, selected on the underside of the brooch bow. Area 1 was large and well cleaned. At both areas, a yellow surface with a metal shine was visible. The areas 3 and 4 represent corrosion; particularly in area 4 there was well-preserved corrosion on the primary surface.

The results of measurements indicate that the brooch was made of brass containing at least 17% zinc. The surface of the brooch was not plated.

Table 16: No. 16. Goriški muzej Nova Gorica, Inv. No. št. 8; *Pl. 1:* 16.
Tab. 16: Št. 16. Goriški muzej Nova Gorica, inv. št. 8; *t. 1:* 16.

Area / Mesto meritve	Description / Opis	Notes / Opombe	Fe	Cu	Zn	Pb	Sn
1	metal core / jedro		0.9	77.7	20.0	0.81	0.5
2	corrosion / korozija	calc. for comp. / rač. za spojine	0.9	54.1	2.2	0.4	1.2
=	=	norm. metals / norm. kovine	1.5	92.0	3.7	0.7	2.1
3	corrosion / korozija	calc. for comp. / rač. za spojine	0.9	52.8	3.9	0.45	1.2
=	=	norm. metals / norm. kovine	1.6	89.1	6.6	0.7	2.0

Commentary:

On area 1, the great majority of corrosion was removed; a yellow surface with a metallic shine was exposed. The unprepared area 2 was selected on the front of the bow, where the corroded primary surface of the brooch was relatively well preserved. The area 3 represented corrosion that was full of small pits.

The results of measurements indicate that the brooch was made of brass containing at least about 20 % zinc. The primary surface of the brooch was not plated.

Table 17: No. 17. Dolenjski muzej, Inv. No. 1256; *Pl. 1:* 17.
Tab. 17: Št. 17. Dolenjski muzej, inv. št. 1256; *t. 1:* 17.

Area / Mesto meritve	Description / Opis	Notes / Opombe	Fe	Cu	Zn	Pb	Bi	Sn
1	metal core, 1st removal of corrosion / jedro, 1. odstr. korozije		2.5	82.0	13.9	0.59		1.0
=	metal core, 2nd removal of corrosion / jedro, 2. odstr. korozije		3.2	79.7	15.5	0.68	0.1	0.9
=	=	repeated measurement / ponovitev mer.	3.6	78.7	16.1	0.67	0.1	0.8

Commentary:

The great majority of corrosion was removed from area 1, selected on the underside of the brooch bow. A yellow surface with a metallic shine could be seen on the cleaned area, but traces of corrosion still remained visible. As the brooch is rather badly preserved, it was not possible to prepare an area completely free of corrosion. For this reason we did not measure the corroded surface.

The results of the measurements, taking into account the remnants of corrosion on the measured area, indicate that the brooch was made of brass, which most probably contained more than 16% zinc.

Table 18: No. 18. Narodni muzej Slovenije, Inv. No. R 24045; *Pl. 1:* 18.
Tab. 18: Št. 18. Narodni muzej Slovenije, inv. št. R 24045; *t. 1:* 18.

Area / Mesto meritve	Description / Opis	Notes / Opombe	Fe	Ni	Cu	Zn	Pb	Bi	Ag	Sn
2	metal core, 1st removal of corrosion / jedro, 1. odstr. korozije		1.4	0.05	81.3	15.4	0.42	0.12		1.4
=	metal core, 2nd removal of corrosion / jedro, 2. odstr. korozije		1.9		79.9	16.6	0.44	0.07	1.1	1.1
=	metal core, 3rd removal of corrosion / jedro, 3. odstr. korozije		1.1		78.2	19.5	0.36			0.9

3	corrosion / korozija	calc. for comp. / rač. za spojine	3.0		49.7	2.2	1.3	0.05	0.2	4.8
=	=	norm. metals / norm. kovine	4.9		81.2	3.6	2.1	0.08	0.3	7.8
4	corrosion / korozija	calc. for comp. / rač. za spojine	4.3		46.7	2.9	1.6	0.05	0.3	6.8
=	=	norm. metals / norm. kovine	6.9		74.5	4.6	2.6	0.08	0.5	10.8

Commentary:

The great majority of corrosion was removed from area 2 (on the underside of the brooch bow); a shiny yellow metallic surface was visible. Areas 3 and 4 were selected on the upper and lower side of the brooch bow, respectively.

The results of measurements indicate that the brooch was made of brass containing at least about 20% zinc. The surface of the brooch was not plated.

Šmit, Istenič

4. SCANNING ELECTRON MICROSCOPY (SEM) AND ENERGY DISPERSIVE X-RAY SPECTROSCOPY (EDX)

Scanning electron microscopy (SEM) allows investigation of the sample surface under large magnifications, and combined with energy dispersive X-ray spectroscopy (EDX), provides semi-quantitative chemical analysis of extremely small surfaces (one tenth of a mm or less is sufficient). Both methods were used for the bronze brooch No. 5 to find out if the high content of tin at the surface is a consequence of tinning or other effects (see above, Sect. 3). For comparison, SEM was also used for investigation of brooch No. 11, which was undoubtedly tinned (compare Sect. 3). The low-vacuum mode of microscopy that does not require a pre-treated sample surface was applied. Backscattered electrons were used for SEM imaging. In this way materials made of heavy elements appear bright in the image, while materials made of light elements are darker.

Surface treatment applying tinning is an old method. It was used for improving the corrosion and mechanical resistance of the surface and for its decoration. Tin with a flux was applied to the heated surface of the object. The flux decomposes the oxides on the surface and enables formation of an adhesion joint. The temperature should be slightly higher than the melting point of tin, i.e. above 231.9°C. Maintaining the object at this increased temperature or heating to even higher temperatures causes diffusion of tin and copper. The primary tin surface disappears and a layer of intermetallic compounds is formed. The ε phase (Cu_3Sn) is the main product, but also some δ phase ($Cu_{31}Sn_8$) is obtained. The effect of this surface treatment is thus production of intermetallic compounds that are resistant to scratching. They are also corrosion-resistant, as they function as a cathode in the corrosion process. Polishing gives them a bright silvery shine. Pure tin would disappear much faster due to corrosion, and the surface would be less brilliant. Beside copper, tinning was also applied to brass and low-grade bronzes. For bronzes containing a larger fraction of tin (19 to 27%), which already contained the δ phase in the form of a eutectoid, the shine was attained by polishing (Meeks 1993).

The corrosion of tinned objects develops by penetration of electrolytes through microcracks and other defects in the hard surface layer to the less noble metal basis. In this process, more voluminous oxides are formed that peel away parts of the tinned surface, so the corrosion of the metal base continues. With the progress of corrosion, only a few areas with preserved tinning remain. On high-grade bronzes that are not tinned and have the eutectoid in microstructure, corrosion proceeds by selective decay of the α phase that contains less tin. As only the more stable δ phase remains in the eutectoid, the surface becomes rough (Meeks 1993).

The corrosion-induced degradation process described above appears in a normal environment characterized by the presence of water or wetness. In a more aggressive corrosion medium that contains clorides and other substances for instance, the corrosion mechanism can also be different.

The brass brooch No. 11 has a relatively well preserved silvery surface. Analysis by SEM EDX showed a thin metal layer containing about 38% Sn, preserved only at particular areas (bright regions in *Fig. 2*). The results of analyses of different parts of this surface gave 35.29 % Sn, 35.10 % Sn, 37.31 % Sn, 38.20 % Sn, 38.84 % Sn, 40.58 % Sn; mean value 37.55 % Sn. The composition of this layer correspons agrees well with the composition of the ε phase (Cu_3Sn), which results from heating to temperatures about 350°C and contains 38.2% tin. These bright regions are encircled by

Fig. 2: Brooches Nos. 12, 13 and 14 with locations of the areas measured at the widening of the oval (photo Tomaž Lauko, Narodni muzej Slovenije).
Sl. 2: Fibule št. 12, 13 in 14 z označenimi mesti meritev PIXE na ovalnih razširitvah (foto: Tomaž Lauko, Narodni muzej Slovenije).

copper oxide. Beside quantitative analysis, surface tinning was confirmed by its appearance in the scanning electron microscope. The areas rich in tin and not oxidized appear markedly bright. Namely, brighter regions contain elements with a larger atomic mass - tin has an atomic mass about 1.8 times larger than copper and zinc. Oxides containing much oxygen appear dark in colour.

The brooch No. 5 does not show any apparent surface tinning. Analyses of the base metal using SEM EDX (area 4) indicate that the brooch was made of bronze containing about 10% tin. Investigations by scanning electron microscopy did not reveal any bright regions that would indicate the presence of corrosion-resistant ε and δ intermetallic compounds, characteristic of tinning of low grade bronzes (*Fig. 3*). The SEM EDX analyses on the surface and of the layer above the base metal showed a relatively high content of tin (12 to 46%).

We consider that the brooch surface was not tinned. It is a characteristic of tin bronzes containing low amounts of tin (below 10%) that a very stable tin oxide remains at the surface, while other oxides dissolve rapidly. The fraction of tin becomes larger and may exceed 60%.

Gerdun, Mladenovič

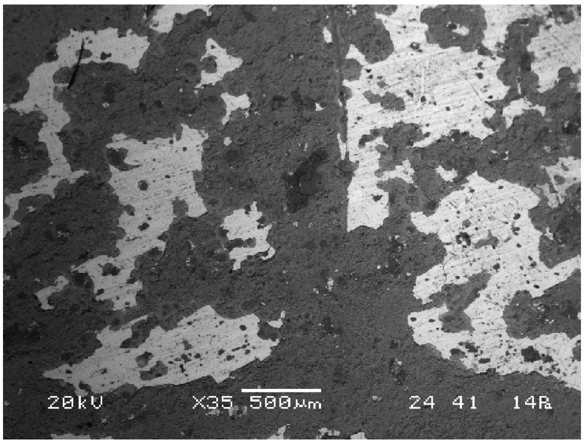

Fig. 3: SEM photograph of the remnants of tinning on the surface of brooch No. 11.
Sl. 3: Ostanki pokositrenja na površini medeninaste fibule št. 11.

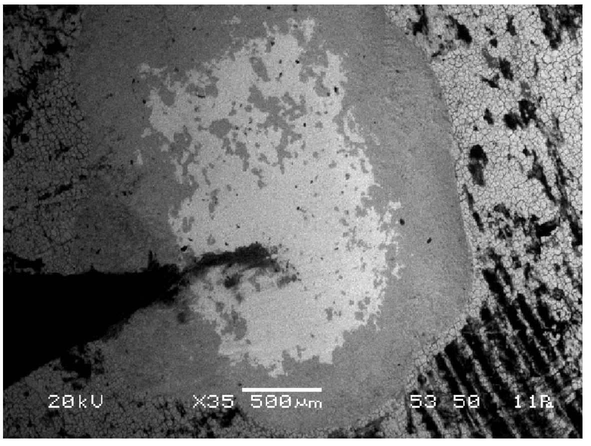

Fig. 4: SEM photograph of prepared area 4 and its surrounding on the surface of brooch No. 5. The bright region in the middle is the metal core, the grey surrounding area represents oxides; intermetallic compounds were not detected.
Sl. 4: Obrušeno mesto (mesto 4) na površini fibule št. 5. Svetlo območje v sredini je kovinsko jedro. Siva okolica predstavlja okside. Na nobenem mestu nismo ugotovili intermetalnih spojin.

5. **CONCLUSIONS**

The majority of the analyzed brooches (14 of 18) are made of brass. One brooch is made of gun metal, i.e. an alloy of copper with tin and zinc (No. 3), and three are made of bronze (Nos. 5-7). The alloy of one of the bronze brooches contains about 1% zinc which probably originates from brass added to bronze as recycled material.

The measurements of corrosion on the surface of the brooches by the method of X-ray fluorescence spectroscopy (XRF) detected zinc in the corroded surface of all brass brooches. The proportionally small fraction of this element detected in the corrosion layer (about 5-6% in the noble type of corrosion, i.e. patina) was expected, since zinc as a less noble metal is preserved badly or not at all in the corrosion (Craddock 1978). The content of zinc was then most precisely determined for the brooch No. 1, as the corrosion layer on the brooch surface was very thin (cf. Istenič 2005, No. 1). X-ray fluorescence did not detect zinc in the brooch No. 3, which was made of gun metal containing about 3% zinc.

Measurements of the corrosion layer using PIXE also showed comparatively small fractions of zinc. On those areas where we gradually and more and more precisely removed the corrosion layer, each subsequent measurement showed a larger fraction of zinc (up to 21%) and smaller amounts of iron (though its determination was relatively inaccurate, compare sect. 2.1), tin and lead. The results of these measurements indicate that the brooches were made of "pure" brass that contained about 20% zinc and a very small amount of lead and tin (cf. Jackson, Craddock 1995, 93; Craddock, Lambert 1985, 164).

Tinning is easily identified on brass (No. 11), but an increased concentration of tin on bronze may result from different causes. Investigations using scanning electron microscopy demonstrated that the increased content of tin in the brooch No. 5 is very likely not a result of tinning.

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Arheometrične analize fibul skupine Alesia s slovenskih najdišč

1. UVOD

Obravnava je zajela osemnajst fibul skupine Alesia s slovenskih najdišč. Zanimalo nas je predvsem, ali so izdelane iz brona, medenine ali rdeče litine (cf. Istenič 2005, 00).

Prisotnost oz. odsotnost cinka v zlitinah, iz katerih so bile izdelane fibule, smo ugotavljali s preiskavo korodirane površine predmetov z metodo rentgenske fluorescenčne spektrometrije (XRF). Natančnejšo sestavo predmetov smo ugotavljali na majhnih površinah predmetov, s katerih smo, kolikor se je dalo dobro, odstranili korozijo. Pripravljena mesta smo izmerili z metodo protonsko vzbujene rentgenske spektrometrije (PIXE). Natančnejše analitske metode, ki so nam bile na razpolago (ICP-AES), namreč zaradi drobnosti (tenkosti) fibul niso primerne. Poleg tega pa so rezultati, pridobljeni s tehniko PIXE, glede na zastavljeno vprašanje dovolj natančni.

Preiskave s pomočjo vrstičnega elektronskega mikroskopa (SEM) in elektronske disperzijske spektroskopije rentgenskih žarkov (EDX) so bile potrebne za interpetacijo visoke vsebnosti kositra na površini fibule št. 5.

Istenič

2. PREISKAVE S TEHNIKO RENTGENSKE FLUORESCENČNE SPEKTROMETRIJE (EDS XRF)

Analize smo izvedli v Narodnem muzeju Slovenije na napravi X-Ray Analyzer Model PEDUZO 01/Am/Sip-250, ki so jo izdelali v Inštitutu Jožef Stefan.[1] Meritev zajame krog s premerom 11 mm in površinsko plast predmeta, saj seže le nekaj deset mikronov (mm) v globino.

Preiskali smo korozijsko plast na površini fibul. Rezultat analize zato ne pokaže sestave zlitine, iz katere je bila fibula izdelana, dovoljuje pa predvidevanje o njeni približni sestavi. Ker nas je zanimalo predvsem, katere fibule so izdelane iz medenine ali rdeče litine, je bila v rezultatu meritev pomembna predvsem prisotnost oz. odsotnost cinka. Zaradi topnosti cinkovih korozijskih produktov smo predvideli, da bo delež cinka v korozijski plasti bistveno manjši kot v kovinskem jedru predmeta.

Od 18 raziskanih fibul je bila prisotnost cinka ugotovljena pri štirinajstih (št. 1, 2, 4, 8-18). Izmerjeni delež cinka je znašal od 5 do 17 %.[2] Pri fibulah št. 3, 5, 6 in 7 cink ni bil ugotovljen.

Milić

3. PROTONSKO VZBUJENA RENTGENSKA SPEKTROMETRIJA (PIXE)

3.1 Opis metode

Meritve smo opravili s tandemskim pospeševalnikom na Institutu Jožef Stefan, pri čemer smo uporabili merilno linijo s protonskim žarkom v zraku. Protone smo pospešili do energije 2,5 MeV, vendar so protoni pri prehodu 8 μm debele aluminijaste folije in 1 cm široke zračne reže izgubili nekaj energije, tako da so zadevali tarčo z energijo približno 2,2 MeV. Tarča je bila orientirana tako, da je njena normala oklepala z vpadno smerjo protonskega žarka kot 22,5°. Enako velik je bil tudi kot med normalo na tarčo in smerjo proti detektorju rentgenskih žarkov. Mesto zadetka protonskega žarka na tarči smo opazovali s scintilatorjem, ki smo ga naredili iz rubinovega prahu in lepilnega traku. Pri namerjanju žarka nam je nagajala paralaksa, zato smo meritev na istem mestu pogosto ponavljali in sklepali iz rezultata, kdaj smo najbolje zadeli pripravljeno mesto.

Za detekcijo rentgenskih žarkov smo uporabili silicij-litijev detektor z energijsko ločljivostjo 160 eV pri 5,9 keV. Med meritvijo smo detektor opremili z aluminijastim absorberjem debeline 0,3 mm. S tako debelim detektorjem smo izboljšali relativno občutljivost za trše rentgenske žarke okoli kositra, tako da je bila detekcijska meja v tem območju 0,1 %. Z debelim absorberjem smo izboljšali tudi ločevanje med arzenovimi črtami K in svinčevimi črtami L, saj smo z absorberjem povečali relativni delež arzenove črte K_β in svinčeve črte L_β v spektru. Najmanjša detekcijska meja za arzen je bila 0,03 %. Šlaba stran debelega absorberja pa je bilo delno prekrivanje železovih črt K z ubežnimi vrhovi bakrovih črt, tako da je bila absolutna napaka pri določanju koncentracije železa okoli 0,5 %. Z absorberjem smo tudi porezali rentgenske črte z energijo, manjšo od 5 keV, to je črte L srebra in kositra in črte K lahkih elementov.

Prisotnost cinka v spektru smo ugotavljali po cinkovi črti K_β. Pri obdelavi spektrov s programom AXIL bi namreč zaradi nesimetrične bakrove črte K_β določili majhen pridelek cinkove črte K_α tudi v vzorcih, ki cinka ne vsebujejo. V čistem bakru bi tako določili navidezno koncentracijo cinka okrog 0,4 %. Kot kriterij za prisotnost cinka v vzorcu smo se zanesli na subjektivno identifikacijo cinkove črte K_β. Detekcijsko mejo za cink je tako smiselno postaviti na okrog 1 %.

Izmerjene jakosti rentgenskih črt smo preračunali v koncentracije (v masnih %) z metodo neodvisnih parametrov (glej npr. Šmit in drugi 2005), to je z znanimi preseki za produkcijo rentgenskih žarkov, z znano zavorno silo protonov in z znanimi atenuacijskimi koeficienti rentgenskih žarkov, kot jih navaja strokovna literatura. Med sekundarnimi učinki pri sevanju rentgenskih žarkov smo upoštevali fluorescenco, ki jo vzbujajo drugi, trši rentgenski žarki v tarči. Kot normalizacijski postopek smo upoštevali, da je vsota vseh masnih deležev v tarči enaka ena, s čimer smo se izognili umerjanju prostorskega kota rentgenskega detektorja in merjenju števila protonov pri vsaki meritvi. Pravilnost postopkov smo preverjali z meritvami medeninastega standarda 1107, ki vsebuje 1,04 % kositra. Standardne vrednosti smo reproducirali z natančnostjo nekaj odstotkov, tako da lahko za natančnost metode privzamemo ±5 %. Pri elementih okoli kositra moramo k tej vrednosti prišteti še statistično napako, ki je bila pri majhnih koncentracijah Sn (~0,3 %) okrog 10 %.

Poleg čistih kovinskih površin smo izmerili tudi nekaj mest, ki jih je prekrivala plast korozijskih produktov. Na teh mestih smo želeli dobiti le informacijo o razmerjih med posameznimi

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[1] Kot vir sevanja smo uporabljali 25 mCi Am-241 radioizotop. Rentgentski spektrometer uporablja Si PIN detektor z ločljivostjo 250 eV pri 5,9 keV. Spekter analizira 1024 kanalni analizator z diferencialno nelinearnostjo < 2 % in integralno nelinearnostjo < 1 %. Detektor je nameščen v vakumu in ima 25 mikronov debelo Be okno. Peltierov hladilnik je vgrajen v ojačevalni sistem in vzdržuje temperaturo 235 °K na PIN diodi. Nastavitev sistema je opravljena že pri sami izdelavi, tako da je spektralno energijsko območje 3-30 keV z razpršitvijo približno 30 eV/kanal.

[2] Št. 1 (17 %), 2 (6 %), 4 (4,6 %), 8 (5 %), 9 (5,6 %), 10 (9,8 %), 11 (10 %), 12 (4 %), 13 (5,4 %), 14 (12,3 %), 15 (6 %), 16 (11,2 %), 17 (6,2 %), 18 (9,3 %).

kovinami, da bi tako odkrili morebitne posrebritve in pokositrenja. Ker z metodo PIXE ne moremo meriti lahkih elementov (kisika, ogljika, vodika), smo privzeli, da so kovine vezane v izbrane kemične spojine, katerih skupni delež je prav tako ena. Za baker smo privzeli, da je vezan v malahit $CuCO_3.Cu(OH)_2$, za druge kovine pa smo predpostavili oksidno obliko. Tipični delež kovin v taki korozijski plasti je okrog 60 %. Za kovinsko komponento smo nato preračunali še relativne deleže, tako da smo vsoto kovinskih koncentracij normirali na 100 %. Tako dobljene vrednosti so se le za nekaj odstotkov razlikovale od vrednosti, ki bi jih dobili z računom za čisto kovino.

3.2 **Opis meritev, rezultati in komentar**

Z metodo PIXE smo merili dve vrsti mest: 1) posebno pripravljene točke na fibulah, s katerih smo v velikosti 2-3 mm^2 skušali čimbolj odstraniti korozijsko plast do kovinskega jedra, in 2) korodirano površino fibul, kjer smo skušali odkriti morebitne sledi nanosa na prvotni površini (npr. posrebritev, pokositrenje itd.; prim. npr. Šmit 2003; Istenič, Milić, Šmit 2003, 291-292). Rezultate meritev na korodiranih mestih smo v preglednicah navedli na dva načina: 1) vsebnost posameznih kovinskih elementov, ki smo jih izračunali kot sestavni del karbonatov in oksidov (v tabeli označeno z 'rač. za spojine'), in 2) vsebnost posameznih kovinskih elementov, ki smo jih dobili z normiranjem vrednosti kovin v spojinah na 100 % (označeno z 'norm. kovine').

Z meritvami mest, s katerih smo odstranili korozijo in tanko vrhnjo kovinsko plast, smo ugotavljali približno sestavo kovinskega jedra fibul. Pregled tako pripravljenih mest pod povečavo je pokazal, da je izredno težko povsem odstraniti korozijo z izbrane površine. V nekaterih primerih je kovinsko jedro tako slabo ohranjeno, da bi popolna odstranitev korozije na dovolj veliki površini predmet preveč poškodovala. Zanesljivost merskih rezultatov pri določanju sestave kovinskega jedra je torej odvisna predvsem od tega, kako temeljito je uspelo korozijo odstraniti in kako dobro je žarek zadel tarčo (mesto, s katerega je bila odstranjena korozija). Zaradi navedenih razlogov smo meritve na nekaterih mestih večkrat ponovili, običajno z dodatnim čiščenjem in/ali s povečevanjem merjene površine. Izrazito majhna mesta smo merili z navadnim žarkom (premer 2 mm) in ozkim žarkom (premer 0,3 mm). V tabelah predstavljene meritve so bile izvedene z navadnim žarkom, če ni drugače navedeno (glej rubriko "opombe"). Podani so le rezultati izbranih meritev, največkrat meritve po prvem in po zadnjem čiščenju merjenega mesta, oziroma meritev, pri katerih je žarek najbolje zadel tarčo. V nekaterih primerih (npr. št. 4, mesto 1) smo zaradi dokumentiranja odvisnosti rezultatov od zgoraj navedenih okoliščin navedli več meritev. Delež cinka se je praviloma po dodatnem čiščenju (tj. odstranitvi korozije) povečal (npr. št. 1, mesti 1 in 2).

Večji del železa (skupaj z delom Sn in Pb), izmerjenega na pripravljenih mestih, najverjetneje izvira iz ostankov patine na očiščenem mestu ali pa iz patine v okolici očiščenega mesta, če žarek ni dobro zadel tarče. Deleži železa so nenatančni do absolutne vrednosti 0,5 %. Natančneje smo jih merili pri meritvah z 0,3 mm zaslonko, saj smo v tem primeru uporabili kot absorber le 100 μm debelo kaptonsko folijo. Koncentracije železa iz teh meritev so zato v tabelah podane z dvema decimalnima mestoma.

Izredno majhni izmerjeni deleži cinka v koroziji na površini medeninastih fibul (npr. št. 2: mesto 3) jasno dokumentirajo neobstojnost tega elementa na površini. Izgubljanje cinka s površine prav tako kaže primerjava med rezultati meritev na korodirani površini in površini, s katere smo odstranili glavnino korozije (npr. št. 2, mesti 1 in 3, št. 3, mesti 1 in 2 itd.).

Pri fibuli št. 12 smo izmerili koncentracijski profil cinka z diferencialno metodo PIXE (Šmit, Holc 2004). Pri tem postopku opravimo vrsto zaporednih meritev z različnimi protonskimi energijami, tako da na izbranem mestu tarče prodremo s protoni do različnih globin. Največja globina, do katere lahko izmerimo profil, je odvisna od dosega protonov pri največji energiji in je običajno manjša od 10 μm. Na površini fibule št. 12 je tenka plast korozije, ki ni nastala na prvotni površini (prim. Istenič 2005). Koncentracija cinka do globine 6 μm je približno 1 % in proti notranjosti počasi narašča (*sl. 1*).

Rezultati meritev so podani v preglednicah. Navedli smo le elemente, ki so v spektrih presegli detekcijsko mejo.

Št. 1 (*tab. 1*)
Komentar:

Na mestih 1 in 2 (na spodnji strani loka) je bila odstranjena glavnina korozije; njuna površina ima rumen kovinski sijaj. Mesti 3 in 4 sta bili izmerjeni na zgornji strani loka na površini fibule, ne da bi odstranili korozijo.

Rezultati meritev na mestih 1 in 2 kažejo, da je bila fibula izdelana iz medenine z najmanj okoli 20 % cinka. Meritve na mestih 3 in 4 le malo odstopajo od meritev na mestih 1 in 2, kar potrjuje, da temnorjava korozijska plast na fibuli ni nastala na prvotni površini, temveč potem, ko je bila prvotna korozijska plast odstranjena (cf. Istenič 2005, št. 1). Omenjeno korozijsko plast je verjetno povzročil nanos kalijevega polisulfida, ki pa ga meritev ni zaznala, ker nismo merili elementov, lažjih od železa.

Št. 2 (*tab. 2*)
Komentar:

Na mestih 1 in 2 je bila odstranjena glavnina korozije, njuna površina ima rumen kovinski sijaj. Mesto 3 predstavlja korozijo na prvotni površini fibule, na zgornji strani loka.

Rezultati meritev kažejo, da je bila fibula izdelana iz medenine z najmanj okoli 21 % cinka. Na površini ni bilo nanosa druge kovine.

Št. 3 (*tab. 3*)
Komentar:

Na mestu 1 je bila odstranjena glavnina korozije, njegova površina ima rjavorumen kovinski sijaj. Točka je bila merjena z navadnim in ožjim žarkom. Na mestu 2 smo merili korozijo na površini fibule.

Rezultati meritev kažejo, da je bila fibula izdelana iz rdeče litine, tj. zlitine bakra (okoli 90 %) s kositrom (okoli 6 %) in cinkom (okoli 3 %). V zlitini je tudi okoli 1 % svinca. Zlitina je lahko nastala tako, da so zlitini brona dodali medeninast predmet ali njegov del, namenjen recikliranju. Na površini ni bilo nanosa druge kovine.

Št. 4 (*tab. 4*)
Komentar:

Na mestih 1 in 2 je bila odstranjena glavnina korozije, njuna površina ima rumen kovinski sijaj. Obe točki sta bili merjeni večkrat. Mesti 3 in 4 ležita na korodirani površini fibule na spodnji oziroma zgornji strani loka.

Rezultati meritev kažejo, da je bila fibula izdelana iz medenine z najmanj okoli 17 % cinka. Razmeroma velik delež železa in kositra najverjetneje izvira iz ostankov korozije na mestih 1 in 2. Meritve korozije ne kažejo, da bi fibula imela kovinsko prevleko.

Št. 5 (*tab. 5*)
Komentar:

Na mestih 2, 3 in 4 je bila odstranjena glavnina korozije. Njihova površina ima rjavordeč kovinski sijaj. Mesti 2 in 3, ki sta razmeroma zelo majhni, sta bili merjeni večkrat. Na mestu 1 je bila merjena korozija, ki je nastala na prvotni površini, na mestu 5 pa korozija, ki je nastala potem, ko se je korozija na prvotni površini odluščila.

Meritve kažejo, da je fibula bronasta. Ker je delež kositra v koroziji (mesto 1) zelo velik in je ponavljanje meritev na mestih 2 in 3 pokazalo, da se vsebnost kositra zmanjša po dodatnem odstranjevanju korozije z merjene točke, sklepamo, da znaša vsebnost kositra v jedru fibule manj kot 13 %.

V koroziji, ki je nastala na prvotni površini, je bil izmerjen visok delež kositra (mesto 1), kar bi lahko bila posledica pokositrenja ali pa korozijskih procesov (cf. Meeks 1993). Pregled fibule z vrstičnim elektronskim mikroskopom je pokazal, da fibula ni bila pokositrena (glej pogl. 4 in *sl. 4*).

Št. 6 (*tab. 6*)
Komentar:
Na mestih 1 in 2 je bila glavnina korozije odstranjena, njuna površina ima rjavordeč kovinski sijaj. Točka 1 je majhna, zato je bila merjena tudi z ozkim žarkom. Mesto 2 je po drugi odstranitvi korozije veliko, še vedno pa so na njem drobne jamice, v katerih je korozija. Mesto 3 predstavlja korozijo na prvotni površini zgornje strani loka fibule.

Rezultati meritve mesta 2 kažejo, da je bila fibula izdelana iz bakrove zlitine, ki je vsebovala manj kot okoli 7 % kositra, 2-3 % svinca in okoli 1 % cinka. Domnevamo, da majhen, a nedvomen delež cinka izvira iz medenine, ki je bila dodana kot material, namenjen recikliranju.

Ker fibula nima srebrno svetleče površine, menimo, da ni bila pokositrena.

Št. 7 (*tab. 7*)
Komentar:
Gladko srebrno se svetlečo plast na površini zgornje strani fibule smo merili na mestu 1, kjer je razmeroma dobro ohranjena, in na mestu 2, kjer je slabše ohranjena. Na mestih 3 in 5 je bila odstranjena glavnina korozije, zato je vidno rjavorumeno svetleče kovinsko jedro. Mesto 3 je bilo merjeno večkrat. Mesto 4 smo izbrali na korodirani površini spodnje strani loka fibule.

Rezultati meritev so pokazali, da je bila fibula narejena iz brona, ki vsebuje okoli 7 % kositra in 5 % svinca. Koncentracija cinka 0,4 %, ki smo jo izmerili pri prvi meritvi mesta 3, je na skrajni detekcijski meji in je nismo ponovili pri meritvi bolje očiščene površine. Prisotnost cinka v kovinskem jedru je torej manjša od detekcijske meje.

Tanka srebrno svetleča plast na površini verjetno predstavlja pokositrenje.

Št. 8 (*tab. 8*)
Komentar:
Na mestih 1 in 2, ki sta bili izbrani na spodnji strani loka, je bila odstranjena glavnina korozije do rumeno se svetlečega kovinskega jedra. Mesto 1 je bistveno večje (4 x 3 mm) in bolje očiščeno. Meritve so bile opravljene večkrat, tudi z malim žarkom. Na mestih 3 in 4, ki ležita na zgornji strani loka, je bila merjena sestava korozije, ki je nastala na prvotni površini fibule.

Rezultati meritev kažejo, da je bila fibula izdelana iz medenine z najmanj okoli 20 % cinka. Na površini ni bilo prevleke.

Št. 9 (*tab. 9*)
Komentar:
Na mestu 1, izbranem na spodnji strani loka fibule, je bila odstranjena glavnina korozije do rumeno se svetlečega kovinskega jedra. Mesto 2 je bilo izbrano na koroziji, ki je nastala na prvotni površini fibule na zgornji strani loka.

Iz rezultatov meritev izhaja, da je bila fibula narejena iz medenine, ki je vsebovala najmanj okoli 15 % cinka. Domnevamo, da je delež cinka večji, kajti razmeroma visok delež železa in kositra kaže, da smo merili tudi ostanke korozije (na pripravljenem mestu), ali pa je žarek zadel tudi korozijo v okolici mesta 1. Na površini fibule najverjetneje ni bilo prevleke.

Št. 10 (*tab. 10*)
Komentar:
Na mestih 1 in 2 (izbranih na spodnji strani loka fibule) je bila odstranjena glavnina korozije do rumeno se svetlečega kovinskega jedra; obe mesti sta bili merjeni večkrat. Mesto 1 je večje in bolje očiščeno. Mesti 3 (na spodnji strani loka fibule) in 4 (na zgornji strani loka fibule) sta bili izbrani na koroziji - mesto 4 na koroziji, ki je morda nastala na slabo ohranjeni prvotni površini.

Rezultati meritev kažejo, da je fibula izdelana iz medenine z najmanj okoli 20 % cinka. Na površini fibule ni sledov prevleke (npr. pokositrenja).

Št. 11 (*tab. 11*)
Komentar:
Točki 1 in 2 sta bili izbrani na različno dobro ohranjeni sijoči srebni plasti na zgornji strani loka fibule. Na mestih 3 (na nogi), 5 in 6 (na spodnji strani loka fibule) je bila odstranjena korozijska plast do rumeno se svetlečega kovinskega jedra. Mesto 4 leži na stranici železne osi tečaja. Mesto 7 je bilo izbrano na spodnji strani loka fibule, na koroziji, ki je verjetno nastala na prvotni površini fibule.

Rezultati meritev kažejo, da je bila fibula narejena iz medenine, ki vsebuje okoli 21 % cinka. Visok delež kositra na mestih 1 in 2 kaže, da je srebrno se svetleča prevleka na zgornji površini fibule pokositrenje. V osnovni zlitini je kositra namreč manj kot odstotek. Primerjaj tudi *sl. 3*.

Št. 12 (*tab. 12*)
Komentar:
Na mestih 1, 2 in 3 (izbranih na spodnji strani loka fibule) je bila odstranjena glavnina korozije do rumeno se svetlečega kovinskega jedra. Mesto 3 je po zadnjem odstranjevanju korozije največje in najbolje očiščeno. Mesto 4 leži na ostanku tanke srebrno svetleče kovinske plasti na zgornji strani fibule, mesto 6 pa na izrazito neravni površini na zgornji strani loka fibule, domnevno na ostankih spajkanja. Na koroziji železa, ki je prekrila del tečaja, smo izbrali mesto 5.

Med rezultati meritev mest 1-3 so najzanesljivejši rezultati zadnje meritve mesta 3. Fibula je torej izdelana iz medenine, ki vsebuje okoli 20 % cinka. Srebrno se svetleča tanka plast na ovalni razširitvi fibule je srebro, ki je bilo na podlago prispajkano z zlitino svinca in kositra (prim. št. 13 in 14).

Št. 13 (*tab. 13*)
Komentar:
Na mestu 1 (na spodnji strani loka fibule) je bila odstranjena glavnina korozije do rumeno se svetlečega kovinskega jedra. Na zgornji strani ovalne razširitve na loku fibule so bila izbrana tri mesta (*sl. 2*): mesti 5 in 7 na najvišje ležeči, "nagubani" plasti, mesto 4 na nižje ležeči površini, ki morda predstavlja ostanke spajkanja, in mesto 3 na gladki površini, ki leži na najnižjem mestu in za katero se zdi, da leži pod plastjo spajkanja; na tem mestu smo odstranili plast korozije, ki je bila zelo tenka - mesto se kovinsko srebrno sveti.

Rezultati zadnjih dveh meritev na mestu 1 kažejo, da je fibula izdelana iz medenine z okoli 18 % cinka. Meritve mest 4, 5 in 7 nakazujejo, da je bila na ovalno razširitev na loku z zlitino kositra in svinca prispajkana srebrna folija (prim. št. 12 in 14).

Št. 14 (*tab. 14*)
Komentar:
Na mestu 1, majhnem in izbranem na nogi fibule, je bila odstranjena glavnina korozije; vidna je kovinsko se svetleča rumena površina. Mesto 3 smo izbrali na zgornji strani ovalne razširitve na loku, kjer je površina izrazito neravna in verjetno predstavlja ostanke spajkanja. Na sprednji strani loka smo merili korodirano površino (mesto 2).

Glede na rezultate meritve na mestu 1 je fibula medeninasta (vsebuje najmanj okoli 21 % cinka). Za spajkanje na ovalni razširitvi (mesto 3) so uporabili zlitino kositra in svinca (prim. št. 12 in 13).

Št. 15 (*tab. 15*)
Komentar:
Na mestih 1 in 2, ki smo ju izbrali na spodnji strani loka fibule, smo odstranili glavnino korozije. Mesto 1 je razmeroma veliko in dobro očiščeno. Na obeh mestih je vidna kovinsko se svetleča rumena površina. Mesti 3 in 4 predstavljata korozijo; predvsem na mestu 4 je dobro ohranjena korozija na prvotni površini fibule.

Rezultati meritev so pokazali, da je bila fibula izdelana iz medenine z najmanj okoli 17 % cinka. Prvotna površina fibule ni imela prevleke (npr. pokositrenja).

Št. 16 (*tab. 16*)
Komentar:
Na mestu 1 smo na majhnem delu površine odstranili glavnino korozije; vidna je kovinsko se svetleča rumena površina. Mesto 2 je bilo izbrano na sprednjem delu loka, kjer je prvotna površina fibule razmeroma dobro ohranjena v koroziji, mesto 3 pa na ovalni razširitvi loka, kjer je korozija jamičasta.

Rezultati meritev kažejo, da je bila fibula izdelana iz medenine, ki vsebuje najmanj okoli 20 % cinka. Na prvotni površini fibule ni bilo prevleke (npr. pokositrenja).

Št. 17 (*tab. 17*)
Komentar:
Na mestu 1, izbranem na spodnji strani loka fibule, smo odstranili glavnino korozije. Na očiščenem delu je vidna kovinsko se svetleča rumena površina, na kateri pa so še vidni ostanki korozije. Zaradi izredno slabe ohranjenosti fibule ni bilo mogoče pripraviti mesta, s katerega bi odstranili vso korozijsko plast. Iz istega razloga tudi nismo merili korodirane površine.

Rezultati meritev ob upoštevanju dejstva, da so bili na merjenem mestu ostanki korozije, kažejo, da je bila fibula izdelana iz medenine, ki je verjetno vsebovala več kot 16 % cinka.

Št. 18 (*tab. 18*)
Komentar:
Na mestu 2 (na spodnji strani loka fibule) smo odstranili glavnino korozije; vidna je rumeno se svetleča površina. Mesti 3 in 4 sta bili izbrani na koroziji na zgornji oziroma spodnji strani loka fibule.

Iz rezultatov meritev izhaja, da je fibula narejena iz medenine z najmanj okoli 20 % cinka.

Šmit, Istenič

4. **VRSTIČNA ELEKTRONSKA MIKROSKOPIJA (SEM) IN ENERGIJSKA DISPERZIJSKA SPEKTROSKOPIJA (EDX)**

Vrstični elektronski mikroskop (SEM) omogoča preiskovanje površine vzorcev pri velikih povečavah, v povezavi z energijsko disperzijsko spektroskopijo (EDX) rentgenskih žarkov pa tudi semikvantitativno kemijsko analizo izredno majhnih površin (zadostuje desetinka mm ali manj). Obe metodi smo uporabili pri bronasti fibuli št. 5, da bi ugotovili, ali je visoka vsebnost kositra na površini posledica pokositrenja ali drugih dejavnikov (glej zgoraj, pogl. 3). Za primerjavo smo z vrstičnim elektronskim mikroskopom pregledali tudi fibulo št. 11, ki je bila nedvomno pokositrena (prim. pogl. 3). Uporabljen je bil nizkovakuumski način mikroskopiranja, pri katerem predhodna obdelava površine vzorca ni potrebna. Slike s SEM so bile posnete z detektorjem odbitih elektronov. Pri tem prikazu so deli materiala, ki ga gradijo težji elementi, svetlejši, deli iz lažjih elementov pa temnejši.

Obdelava površine predmetov z nanašanjem kositra je že zelo stara metoda. Uporabljali so jo za izboljšanje korozijske in mehanske obstojnosti površine ter za njeno dekoracijo. Kositer so ob uporabi talila nanašali na ogreto površino predmeta. Talilo je razgradilo okside na površini in omogočilo tvorbo adhezijske vezi. Temperature so bile nekoliko višje od tališča kositra, to je nad 231,9 °C. Z zadrževanjem na povišani temperaturi ali pa ogretjem do še višjih temperatur je prišlo do difuzije bakra in kositra. Pri tem je izginila prvotna kositrova plast in nastala je plast intermetalnih spojin. Večinoma je nastajala faza ε (Cu_3Sn), v manjši meri pa tudi δ ($Cu_{31}Sn_8$). Pomen takšne toplotne obdelave je bil v tem, da so nastale trde intermetalne spojine, ki so bile odporne na razenje. Zanje je tudi značilno, da so dobro korozijsko obstojne oziroma delujejo kot katoda v korozijskem procesu. Pri poliranju dobijo bleščeč srebrnkast sijaj. Čisti kositer bi korozijsko hitro propadel, površina bi bila tudi manj bleščeča. Poleg bakra so kositrili večinoma medenine in nizko legirane brone. Pri bronih z več kositra (19 % do 27 %), ki so že vsebovali fazo δ v obliki evtektoida in so bili bolj trdi, so dosegli sijaj s poliranjem (Meeks 1993).

Pri pokositrenih predmetih se je korozija razvijala tako, da je skozi mikrorazpoke ali druge napake v trdi površinski plasti vdiral elektrolit do manj plemenite kovinske osnove, ki je bila anodna. Pri tem so nastajali voluminozni oksidi, ki so lahko odluščili del pokositrene plasti in osnovna kovina je korodirala naprej. Z napredovanjem korozije so ostajala samo še posamezna mesta z ohranjenim pokositrenjem. Pri bolj legiranih bronih, ki niso bili pokositreni in so imeli v mikrostrukturi evtektoid, se je korozija razvijala s selektivnim propadanjem s kositrom manj bogate faze α. Ostajala je bolj stabilna faza δ v evtektoidu. Površina je postajala hrapava (Meeks 1993).

Opisana korozijska degradacija se pojavlja v običajnem okolju, kjer je prisotna voda ali vlaga. Pri agresivnejših korozijskih medijih, ki vsebujejo na primer kloride ali druge snovi, je mehanizem lahko drugačen.

Medeninasta fibula št. 11 ima razmeroma dobro ohranjeno srebrnkasto površino. Analize z SEM EDX so pokazale, da gre za pokositreno plast z okoli 38 % Sn, ki se je ohranila samo na posameznih mestih (svetla območja na sliki 2). Rezultati analiz na več mestih te površine so bili 35,29 % Sn, 35,10 % Sn, 37,31 % Sn, 38,20 % Sn, 38,84 % Sn, 40,58 % Sn; povprečna vrednost 37,55 % Sn). Sestava te plasti se relativno dobro ujema s sestavo faze ε (Cu_3Sn), ki nastane pri segrevanju na temperaturo okrog 350 °C in vsebuje 38,2 % kositra. Okoli svetlih območij se pojavlja predvsem bakrov oksid. Pokositrenje površine potrjuje poleg kvantitativne analize tudi njen videz pod vrstičnim elektronskim mikroskopom. Mesta, ki so bogata s kositrom in niso oksidi, so videti izrazito svetla. Svetlejša mesta namreč vsebujejo elemente z večjo molsko maso - kositer pa ima približno 1,8-krat večjo molsko maso kot baker ali cink. Oksidi, ki vsebujejo veliko kisika, so temne barve.

Fibula št. 5 na površini ne kaže očitnih znakov pokositrenja. Analize SEM EDX kovinske osnove (mesto 4) nakazujejo, da je bila izdelana iz brona z okoli 10 % Sn. Pri pregledovanju pod vrstičnim elektronskim mikroskopom na nobenem mestu nismo ugotovili zelo svetlih območij, ki bi indicirala prisotnost korozijsko obstojnih intermetalnih spojin ε in δ, značilnih za pokositrenje manj legiranih bronov (*sl. 3*). Analize SEM EDX na površini in v plasti nad kovinsko osnovo so pokazale relativno visoko vsebnost kositra (12 % do 46 %).

Menimo, da površina fibule ni bila pokositrena. Za korozijo kositrovih bronov z nižjo vsebnostjo kositra (pod 10 %) je značilno, da se na površini ohranja zelo stabilen kositrov oksid, medtem ko se drugi oksidi hitreje odtapljajo. Kot posledica se pojavi povečanje kositra, ki lahko doseže 60 %.

Gerdun, Mladenovič

5. **SKLEP**

Velika večina, tj. 14 od 18 analiziranih fibul, je medeninastih. Ena fibula je narejena iz rdeče litine, tj. zlitine bakra s kositrom in cinkom (št. 3), in tri iz brona (št. 5-7). Zlitina ene izmed bronastih fibul (št. 6) vsebuje okoli 1 % cinka, ki verjetno izvira iz medenine, ki je bila bronu dodana kot material, namenjen ponovni uporabi (recikliranju).

Meritve korozije na površini fibul z metodo rentgenske fluorescenčne spektrometrije (EDS XRF) so zaznale cink na korodirani površini vseh medeninastih fibul. razmeroma majhen izmerjeni delež tega elementa v koroziji (okoli 5-6 % pri dobri žlahtni koroziji, tj. patini) je pričakovan, saj se cink kot manj plemenit element v koroziji slabo ali pa sploh ne ohrani (Craddock 1978). Delež cinka je bil zato najbolj natančno določen pri fibuli št. 1, kjer je korozijska plast na površini fibule izredno tenka (prim. Istenič 2005, št. 1). Pri fibuli št. 3, ki je bila narejena iz rdeče litine z okoli 3 % cinka, pa z metodo rentgenske fluorescenčne spektrometrije cinka nismo zaznali.

Meritve korozije na medenini s tehniko PIXE so prav tako pokazale razmeroma majhne deleže cinka. Na mestih, s katerih smo postopoma vse bolj natančno odstranjevali korozijo, so meritve po vsakem dodatnem odstranjevanju ostankov korozije pokazale večjo vrednost cinka (do 21 %) ter nižje vrednosti železa (čeprav je bil ta izmerjen razmeroma nenatančno - prim. pogl. 2.1), kositra in svinca. Rezultati teh meritev torej kažejo, da so bile fibule narejene iz "čiste medenine, ki je vsebovala okoli 20 % cinka ter zelo malo svinca in kositra (cf. Jackson, Craddock 1995, 93; Craddock, Lambert 1985, 164).

Na medenini je pokositrenje lahko ugotoviti (št. 11), na bronu pa ima povišan delež kositra lahko več vzrokov. Preiskave z vrstičnim elektronskim mikroskopom so pokazale, da pri fibuli št. 5 povišan delež kositra verjetno ni posledica pokositrenja.

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