Archaeometric analysis of Alesia group brooches from sites in Slovenia

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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. 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%. No zinc was found in the brooches Nos. 3, 5, 6 and 7.

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° 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 Kβ lines and lead Lβ 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 Kβ zinc line. When treating the spectra with the AXIL program, the asymmetric copper Kβ line gave a small apparent intensity of the zinc Kα 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 Kβ 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...
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, Milič, 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; PI. 1: 1.

<table>
<thead>
<tr>
<th>Area / Mesto meritve</th>
<th>Description / Opis</th>
<th>Notes / Opombe</th>
<th>Fe</th>
<th>Cu</th>
<th>Zn</th>
<th>As</th>
<th>Pb</th>
<th>Ag</th>
<th>Sn</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>metal core, 1st removal of corrosion / jedro, 1. odstr. korozije</td>
<td>1.2 79.1 19.0 0.05 0.22 0.1 0.4</td>
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<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>metal core, 2nd removal of corrosion / jedro, 2. odstr. korozije</td>
<td>1.2 78.2 19.9 0.36 0.4</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>metal core, 1st removal of corrosion / jedro, 1. odstr. korozije</td>
<td>81.6 17.6 0.19 0.1 0.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>metal core, 2nd removal of corrosion / jedro, 2. odstr. korozije</td>
<td>1.1 78.4 19.8 0.31 0.1 0.4</td>
<td></td>
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<table>
<thead>
<tr>
<th>Area / Mesto meritve</th>
<th>Description / Opis</th>
<th>Notes / Opombe</th>
<th>Fe</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
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<th>Sn</th>
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<td>3.4 76.6 15.6 0.05 1.5 0.2 2.6</td>
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</tr>
<tr>
<td>2</td>
<td>metal core, 2nd removal of corrosion / jedro, 2. odstr. korozije</td>
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<td>3</td>
<td>metal core, 1st removal of corrosion / jedro, 1. odstr. korozije</td>
<td>2.3 79.2 15.2 0.04 0.98 0.2 2.0</td>
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<tr>
<td>4</td>
<td>metal core, 2nd removal of corrosion / jedro, 2. odstr. korozije</td>
<td>1.7 0.1 76.0 21.0 0.53 0.8</td>
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</tbody>
</table>

Commentary:
The corrosion was removed from areas 1 and 2; the respective surface shows a yellow metallic shine. Area 3 represents corrosion on the surface of the brooch, on the upper side of the bow.

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

<table>
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<th>Description / Opis</th>
<th>Notes / Opombe</th>
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<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
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<th>Pb</th>
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<td>metal core, 1st removal of corrosion / jedro, 1. odstr. korozije</td>
<td>1.2 79.1 19.0 0.05 0.22 0.1 0.4</td>
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<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>2</td>
<td>metal core, 2nd removal of corrosion / jedro, 2. odstr. korozije</td>
<td>1.2 78.2 19.9 0.36 0.4</td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>metal core, 1st removal of corrosion / jedro, 1. odstr. korozije</td>
<td>81.6 17.6 0.19 0.1 0.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>metal core, 2nd removal of corrosion / jedro, 2. odstr. korozije</td>
<td>1.1 78.4 19.8 0.31 0.1 0.4</td>
<td></td>
<td></td>
<td></td>
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</table>

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.
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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.

<table>
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<tr>
<th>Area / Mesto meritve</th>
<th>Description / Opis</th>
<th>Notes / Opombe</th>
<th>Fe</th>
<th>Cu</th>
<th>Zn</th>
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<th>Pb</th>
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<th>Sn</th>
</tr>
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<td>metal core / jedro</td>
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<td>0.3</td>
<td>90.0</td>
<td>3.1</td>
<td>0.09</td>
<td>1.1</td>
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<td></td>
<td></td>
<td>0.8</td>
<td>88.1</td>
<td>3.1</td>
<td>0.15</td>
<td>1.2</td>
<td>6.8</td>
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<tr>
<td>2</td>
<td>corrosion / korozija</td>
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<td>1.5</td>
<td>52.3</td>
<td>0.7</td>
<td>0.6</td>
<td>0.4</td>
<td>3.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>norm. metals / norm. kovine</td>
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<td>2.6</td>
<td>88.0</td>
<td>1.2</td>
<td>1.0</td>
<td>0.7</td>
<td>6.5</td>
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</tbody>
</table>

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.

<table>
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<tr>
<th>Area / Mesto meritve</th>
<th>Description / Opis</th>
<th>Notes / Opombe</th>
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<th>Cu</th>
<th>Zn</th>
<th>Pb</th>
<th>Ag</th>
<th>Sn</th>
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<td>82.0</td>
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<td>1.2</td>
<td>80.5</td>
<td>16.9</td>
<td>0.25</td>
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<td>1.4</td>
<td>81.5</td>
<td>15.5</td>
<td>0.27</td>
<td>0.06</td>
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<td></td>
<td>1.2</td>
<td>81.0</td>
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<td>0.9</td>
<td>81.9</td>
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<td>1.1</td>
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<td>metal core, 1st removal of corrosion / jedro, 1. odstr. korozije</td>
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<td>83.7</td>
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<td>1.2</td>
<td>81.4</td>
<td>15.9</td>
<td>0.30</td>
<td>1.2</td>
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<tr>
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<td>corrosion / korozija</td>
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<td>45.5</td>
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<td>0.3</td>
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<td>norm. metals / norm. kovine</td>
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<td>9.3</td>
<td>71.6</td>
<td>6.1</td>
<td>2.1</td>
<td>0.5</td>
<td>10.4</td>
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<td>4</td>
<td></td>
<td></td>
<td>6.6</td>
<td>44.1</td>
<td>3.6</td>
<td>1.3</td>
<td>0.3</td>
<td>8.4</td>
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<tr>
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<td>10.3</td>
<td>68.6</td>
<td>5.6</td>
<td>2.0</td>
<td>0.5</td>
<td>13.1</td>
</tr>
</tbody>
</table>

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.

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).


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 con-
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Tab. 7. Št. 7. Narodni muzej Slovenije, inv. št. R 1464; t. 1: 7.

Tab. 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, 1st odstr. korozije | | 1.0 | 0.2 | 86.4 | 0.4 | 0.25 | 4.3 | 7.4 |
4 | repeated measurement / ponovitev mer. | | 0.9 | 0.2 | 86.8 | 0.19 | 4.8 | 0.1 | 7.0 |
5 | metal core, 2nd removal of corrosion / jedro, 2nd odstr. korozije | | 1.8 | 81.7 | 15.0 | 0.78 | 0.7 |
6 | normal metal / norm. kovine | | 4.4 | 58.2 | 10.7 | 26.7 |
7 | 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.


Tab. 8. Area / Mesto / Meritve | Description / Opis | Notes / Opombe | Fe | 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, 1st odstr. korozije | | 1.0 | 0.2 | 86.4 | 0.4 | 0.25 | 4.3 | 7.4 |
4 | repeated measurement / ponovitev mer. | | 0.9 | 0.2 | 86.8 | 0.19 | 4.8 | 0.1 | 7.0 |
5 | normal metal / norm. kovine | | 4.4 | 58.2 | 10.7 | 26.7 |
6 | metal core / jedro | | 1.4 | 0.2 | 82.2 | 0.32 | 6.2 | 9.6 |

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

<table>
<thead>
<tr>
<th>Area / Mesto meritve</th>
<th>Description / Opis</th>
<th>Notes / Opombe</th>
<th>Fe</th>
<th>Cu</th>
<th>Zn</th>
<th>As</th>
<th>Pb</th>
<th>Ag</th>
<th>Sn</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>metal core / jedro</td>
<td></td>
<td>1.6</td>
<td>79.2</td>
<td>15.4</td>
<td>0.86</td>
<td>0.1</td>
<td>2.8</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>corrosion / korozija</td>
<td>calc. for comp. / rač. za spojine</td>
<td>5.5</td>
<td>46.4</td>
<td>1.7</td>
<td>0.6</td>
<td>0.2</td>
<td>6.7</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>metal core, 1st removal of corrosion / jedro, 1. odstr. korozije</td>
<td></td>
<td>0.10</td>
<td>79.2</td>
<td>19.9</td>
<td>0.01</td>
<td>0.28</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>metal core, 2nd removal of corrosion / jedro, 2. odstr. korozije</td>
<td></td>
<td>0.9</td>
<td>80.6</td>
<td>17.7</td>
<td>0.26</td>
<td>0.06</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>metal core, 1st removal of corrosion / jedro, 1. odstr. korozije</td>
<td></td>
<td>1.3</td>
<td>0.06</td>
<td>79.0</td>
<td>18.8</td>
<td>0.26</td>
<td>0.09</td>
<td>0.5</td>
</tr>
<tr>
<td>2</td>
<td>metal core, 2nd removal of corrosion / jedro, 2. odstr. korozije</td>
<td></td>
<td>1.8</td>
<td>53.6</td>
<td>14.4</td>
<td>1.4</td>
<td>0.1</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>corrosion / korozija</td>
<td>calc. for comp. / rač. za spojine</td>
<td>3.0</td>
<td>48.9</td>
<td>2.2</td>
<td>4.8</td>
<td>0.3</td>
<td>2.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>norm. metals / norm. kovine</td>
<td></td>
<td>4.8</td>
<td>78.7</td>
<td>3.5</td>
<td>7.8</td>
<td>0.5</td>
<td>4.7</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>corrosion / korozija</td>
<td>calc. for comp. / rač. za spojine</td>
<td>3.0</td>
<td>90.1</td>
<td>2.4</td>
<td>2.4</td>
<td>0.1</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>norm. metals / norm. kovine</td>
<td></td>
<td>4.0</td>
<td>86.0</td>
<td>4.3</td>
<td>2.9</td>
<td>2.8</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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.

Table 10: No. 10. Narodni muzej Slovenije, Inv. No. R 17319; Pl. 1: 10.

<table>
<thead>
<tr>
<th>Area / Mesto meritve</th>
<th>Description / Opis</th>
<th>Notes / Opombe</th>
<th>Fe</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
<th>As</th>
<th>Pb</th>
<th>Bi</th>
<th>Ag</th>
<th>Sn</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>metal core, 1st removal of corrosion / jedro, 1. odstr. korozije</td>
<td></td>
<td>1.7</td>
<td>80.0</td>
<td>17.5</td>
<td>0.27</td>
<td>0.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>metal core, 2nd removal of corrosion / jedro, 2. odstr. korozije</td>
<td></td>
<td>0.01</td>
<td>79.2</td>
<td>19.9</td>
<td>0.01</td>
<td>0.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>calc. for comp. / rač. za spojine</td>
<td></td>
<td>0.9</td>
<td>80.6</td>
<td>17.7</td>
<td>0.26</td>
<td>0.06</td>
<td>0.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>norm. metals / norm. kovine</td>
<td></td>
<td>1.3</td>
<td>0.06</td>
<td>79.0</td>
<td>18.8</td>
<td>0.26</td>
<td>0.09</td>
<td>0.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>calc. for comp. / rač. za spojine</td>
<td></td>
<td>1.8</td>
<td>53.6</td>
<td>14.4</td>
<td>1.4</td>
<td>0.1</td>
<td>1.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>norm. metals / norm. kovine</td>
<td></td>
<td>3.0</td>
<td>90.1</td>
<td>2.4</td>
<td>2.4</td>
<td>0.1</td>
<td>2.0</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
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.

<table>
<thead>
<tr>
<th>Area / Mesto meritve</th>
<th>Description / Opis</th>
<th>Notes / Opombe</th>
<th>Fe</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
<th>As</th>
<th>Pb</th>
<th>Ag</th>
<th>Sn</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>&quot;silvery&quot; surface, not well preserved / &quot;srebrna&quot; površina, slabše ohr</td>
<td></td>
<td>4.8</td>
<td>78.6</td>
<td>7.2</td>
<td>0.79</td>
<td>0.4</td>
<td>8.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>&quot;silvery&quot; surface, well preserved / &quot;srebrna&quot; površina, dobro ohr.</td>
<td></td>
<td>2.1</td>
<td>72.3</td>
<td>8.9</td>
<td>0.52</td>
<td>16.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>metal core / jedro</td>
<td></td>
<td>0.6</td>
<td>79.6</td>
<td>19.1</td>
<td>0.16</td>
<td>0.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>hinge axis / os tečaja</td>
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<td>92.2</td>
<td>6.6</td>
<td>1.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>metal core, 1° removal of corrosion / jedro, 1. odstr. korozije</td>
<td></td>
<td>1.4</td>
<td>79.4</td>
<td>18.0</td>
<td>0.30</td>
<td>0.1</td>
<td>0.8</td>
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<td></td>
</tr>
<tr>
<td>6</td>
<td>metal core, 2° removal of corrosion / jedro, 2. odstr. korozije</td>
<td></td>
<td>1.4</td>
<td>77.1</td>
<td>20.6</td>
<td>0.33</td>
<td>0.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>corrosion / korozija</td>
<td></td>
<td>0.1</td>
<td>0.7</td>
<td>0.8</td>
<td>0.9</td>
<td>0.6</td>
<td>2.3</td>
<td>3.7</td>
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</tr>
<tr>
<td>8</td>
<td>=</td>
<td></td>
<td>10.2</td>
<td>81.2</td>
<td>3.6</td>
<td>0.03</td>
<td>0.91</td>
<td>0.3</td>
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<td></td>
</tr>
</tbody>
</table>

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.

<table>
<thead>
<tr>
<th>Area / Mesto meritve</th>
<th>Description / Opis</th>
<th>Notes / Opombe</th>
<th>Fe</th>
<th>Cu</th>
<th>Zn</th>
<th>As</th>
<th>Pb</th>
<th>Ag</th>
<th>Sn</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>metal core / jedro</td>
<td></td>
<td>1.2</td>
<td>81.1</td>
<td>16.6</td>
<td>0.26</td>
<td>0.1</td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>metal core / jedro</td>
<td></td>
<td>1.6</td>
<td>80.3</td>
<td>17.1</td>
<td>0.33</td>
<td>0.05</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>metal core, 1° removal of corrosion / jedro, 1. odstr. korozije</td>
<td></td>
<td>1.5</td>
<td>80.5</td>
<td>16.8</td>
<td>0.41</td>
<td>0.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>&quot;silvery&quot; sheath / &quot;srebrna&quot; folija</td>
<td></td>
<td>0.6</td>
<td>78.1</td>
<td>20.4</td>
<td>0.39</td>
<td>0.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>corrosion around the hinge axis / korozija ob osi</td>
<td></td>
<td>0.5</td>
<td>5.5</td>
<td>0.3</td>
<td>0.2</td>
<td>4.9</td>
<td>79.1</td>
<td>9.9</td>
</tr>
<tr>
<td>6</td>
<td>=</td>
<td></td>
<td>53.3</td>
<td>12.4</td>
<td>0.6</td>
<td>0.7</td>
<td>0.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>=</td>
<td></td>
<td>79.0</td>
<td>18.4</td>
<td>0.9</td>
<td>1.0</td>
<td>0.7</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
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>
<thead>
<tr>
<th>Area / Mesto meritve</th>
<th>Description / Opis</th>
<th>Notes / Opombe</th>
<th>Fe</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
<th>Pb</th>
<th>Bi</th>
<th>Ag</th>
<th>Sn</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>metal core, 1. odstr. korozije</td>
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<td>1.3</td>
<td>84.5</td>
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<td>0.28</td>
<td>0.1</td>
<td>0.4</td>
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</tr>
<tr>
<td>1</td>
<td>metal core, 2. odstr. korozije</td>
<td></td>
<td>1.7</td>
<td>81.2</td>
<td>16.4</td>
<td>0.24</td>
<td>0.06</td>
<td>0.3</td>
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<td></td>
</tr>
<tr>
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<td>metal core, 3. odstr. korozije</td>
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<td></td>
<td>81.5</td>
<td>17.9</td>
<td>0.34</td>
<td>0.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>=</td>
<td>repeated measurement / ponovitev mer.</td>
<td></td>
<td></td>
<td>81.5</td>
<td>17.8</td>
<td>0.31</td>
<td>0.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>smooth &quot;silvery&quot; area, corrosion removed / gladka &quot;srebrna&quot; površina, korozija odstranjena</td>
<td></td>
<td>1.2</td>
<td>51.6</td>
<td>1.6</td>
<td>0.39</td>
<td>3.5</td>
<td>41.7</td>
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<td></td>
</tr>
<tr>
<td>=</td>
<td>repeated measurement / ponovitev mer.</td>
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<td>0.8</td>
<td>50.0</td>
<td>1.8</td>
<td>0.61</td>
<td>4.8</td>
<td>41.9</td>
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<td></td>
</tr>
<tr>
<td>4</td>
<td>remains of soldering / ostanki spajkanja</td>
<td>calc. for comp. / rač. za spojine</td>
<td>2.9</td>
<td>46.2</td>
<td>2.3</td>
<td>3.0</td>
<td>1.0</td>
<td>6.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>=</td>
<td>norm. metals / norm. kovine</td>
<td></td>
<td>4.7</td>
<td>74.5</td>
<td>3.7</td>
<td>4.8</td>
<td>1.6</td>
<td>10.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>remains of &quot;silvery&quot; sheath with soldering beneath it / ostanki &quot;srebrne&quot; folije na spajkanju</td>
<td>calc. for comp. / rač. za spojine</td>
<td>1.9</td>
<td>5.83</td>
<td>1.25</td>
<td>11.2</td>
<td>7.4</td>
<td>58.3</td>
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<td></td>
</tr>
<tr>
<td>=</td>
<td>norm. metals / norm. kovine</td>
<td></td>
<td>2.2</td>
<td>6.79</td>
<td>1.46</td>
<td>13.0</td>
<td>8.6</td>
<td>67.9</td>
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<td></td>
</tr>
<tr>
<td>6</td>
<td>corrosion / korozija</td>
<td>calc. for comp. / rač. za spojine</td>
<td>2.5</td>
<td>51.4</td>
<td>3.2</td>
<td>0.95</td>
<td>0.1</td>
<td>1.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>=</td>
<td>norm. metals / norm. kovine</td>
<td></td>
<td>4.2</td>
<td>86.1</td>
<td>5.4</td>
<td>1.6</td>
<td>0.1</td>
<td>2.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>remains of &quot;silvery&quot; sheath with soldering beneath it / ostanki &quot;srebrne&quot; folije na spajkanju</td>
<td>calc. for comp. / rač. za spojine</td>
<td>0.7</td>
<td>2.90</td>
<td>2.02</td>
<td>9.2</td>
<td>13.1</td>
<td>53.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>=</td>
<td>norm. metals / norm. kovine</td>
<td></td>
<td>0.8</td>
<td>3.54</td>
<td>2.47</td>
<td>11.3</td>
<td>16.0</td>
<td>65.9</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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.

<table>
<thead>
<tr>
<th>Area / Mesto meritve</th>
<th>Description / Opis</th>
<th>Notes / Opombe</th>
<th>Fe</th>
<th>Cu</th>
<th>Zn</th>
<th>Pb</th>
<th>Ag</th>
<th>Sn</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>metal core / jedro</td>
<td></td>
<td>1.2</td>
<td>79.9</td>
<td>18.1</td>
<td>0.21</td>
<td>0.06</td>
<td>0.5</td>
</tr>
<tr>
<td>1</td>
<td>metal core / jedro, narrow beam / ozek žarek</td>
<td></td>
<td>0.17</td>
<td>78.1</td>
<td>21.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>corrosion / korozija</td>
<td>calc. for comp. / rač. za spojine</td>
<td>7.0</td>
<td>44.9</td>
<td>5.0</td>
<td>3.8</td>
<td>0.1</td>
<td>1.2</td>
</tr>
<tr>
<td>3</td>
<td>remains of soldering / ostanke spajkanja</td>
<td>calc. for comp. / rač. za spojine</td>
<td>6.21</td>
<td>2.33</td>
<td>15.1</td>
<td>55.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>remains of soldering / ostanke spajkanja</td>
<td>norm. metals / norm. kovine</td>
<td>7.89</td>
<td>2.96</td>
<td>19.1</td>
<td>70.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**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.

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

<table>
<thead>
<tr>
<th>Area / Mesto meritve</th>
<th>Description / Opis</th>
<th>Notes / Opombe</th>
<th>Fe</th>
<th>Cu</th>
<th>Zn</th>
<th>Pb</th>
<th>Sn</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>metal core / jedro</td>
<td></td>
<td>0.9</td>
<td>77.7</td>
<td>20.0</td>
<td>0.81</td>
<td>0.5</td>
</tr>
<tr>
<td>2</td>
<td>corrosion / korozija</td>
<td>calc. for comp. / rač. za spojine</td>
<td>0.9</td>
<td>54.1</td>
<td>2.2</td>
<td>0.4</td>
<td>1.2</td>
</tr>
<tr>
<td>3</td>
<td>corrosion / korozija</td>
<td>calc. for comp. / rač. za spojine</td>
<td>0.9</td>
<td>52.8</td>
<td>3.9</td>
<td>0.45</td>
<td>1.2</td>
</tr>
<tr>
<td>4</td>
<td>corrosion / korozija</td>
<td>calc. for comp. / rač. za spojine</td>
<td>0.9</td>
<td>54.1</td>
<td>2.2</td>
<td>0.4</td>
<td>1.2</td>
</tr>
</tbody>
</table>

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.

<table>
<thead>
<tr>
<th>Area / Mesto meritve</th>
<th>Description / Opis</th>
<th>Notes / Opombe</th>
<th>Fe</th>
<th>Cu</th>
<th>Zn</th>
<th>Pb</th>
<th>Bi</th>
<th>Sn</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>metal core, 1st removal of corrosion / jedro, 1. odstr. korozije</td>
<td></td>
<td>2.5</td>
<td>82.0</td>
<td>13.9</td>
<td>0.59</td>
<td>0.1</td>
<td>1.0</td>
</tr>
<tr>
<td>2</td>
<td>metal core, 2nd removal of corrosion / jedro, 2. odstr. korozije</td>
<td></td>
<td>3.2</td>
<td>79.7</td>
<td>15.5</td>
<td>0.68</td>
<td>0.1</td>
<td>0.9</td>
</tr>
<tr>
<td>3</td>
<td>metal core, 3rd removal of corrosion / jedro, 3. odstr. korozije</td>
<td></td>
<td>1.1</td>
<td>78.2</td>
<td>19.5</td>
<td>0.36</td>
<td>0.2</td>
<td>0.9</td>
</tr>
</tbody>
</table>

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.

<table>
<thead>
<tr>
<th>Area / Mesto meritve</th>
<th>Description / Opis</th>
<th>Notes / Opombe</th>
<th>Fe</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
<th>Pb</th>
<th>Bi</th>
<th>Ag</th>
<th>Sn</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>metal core, 1st removal of corrosion / jedro, 1. odstr. korozije</td>
<td></td>
<td>1.4</td>
<td>0.05</td>
<td>81.3</td>
<td>15.4</td>
<td>0.42</td>
<td>0.12</td>
<td>1.4</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>metal core, 2nd removal of corrosion / jedro, 2. odstr. korozije</td>
<td></td>
<td>1.9</td>
<td>0.05</td>
<td>79.9</td>
<td>16.6</td>
<td>0.44</td>
<td>0.07</td>
<td>1.1</td>
<td>1.1</td>
</tr>
<tr>
<td>4</td>
<td>metal core, 3rd removal of corrosion / jedro, 3. odstr. korozije</td>
<td></td>
<td>1.1</td>
<td>0.05</td>
<td>78.2</td>
<td>19.5</td>
<td>0.36</td>
<td>0.2</td>
<td>0.9</td>
<td></td>
</tr>
</tbody>
</table>
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 chlorides 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 corresponds 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
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.](image)

**Fig. 3:** SEM photograph of the remnants of tinning on the surface of brooch No. 11.

**Sl. 3:** Ostanke pokositrenja na površini medeninaste fibule št. 11.
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.

CRADDOCK, P. T. 1978, The Composition of the Copper Alloys used by the Greek, Etruscan and Roman Civilizations. 3. The Origins and Early Use of Brass. - Journal of Archaeological Science 5, 1-16.

CRADDOCK, P. T. and J. LAMBERT 1985, The Composition of the Trappings. - In: I. Jenkins, A Group of Silvered-Bronze Horse-Trappings from Xanten (Castra Vetera), Britannia 16, 141-164.


Arheometrične analize fibul skupine Alesia s slovenskih najdišč

1. UVOD

Obhravnava 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. odzotnost cinka v zlitinah, iz katerih so bile izdelane fibule, smo ugotavljali s preiskavo korodirane površine predmetov z metodo rentgenske fluoresčne spektrometrije (XRF). Natančnejše sestavo predmetov smo izmerili z metodico protonsko vzbujene rentgenske spektrometrije (PIXE).

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

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

Rezultate analize ni izvedlo zdaj in proizvedenje pravilno in statistično pravilno, pri katerem je najboljši rezultat potekal v primerjavi z standardom 1107, ki vsebuje 1,04 % kositra. Standardne vrednosti smo preverjali z meritvami medeninaste poljskega detektorja in merjenju števila protonov pri vsaki meritvi. Standardne vrednosti črte Kβ di nesimetrične bakrove črte Kβ in svinčevimi črtami L, saj smo z absorberjem povečali relativni delež arzenove črte Kα in svinčevih črt L, saj smo z absorberjem povečali relativni delež arzenove črte Kα.

3. PROTONSKO VZBUJENA RENTGENSKA SPEKTROMETRIJA (PIXE)

Meritev smo opravili na zaporedni podstavek na Institutu Jožef Stefan, pri čemer smo uporabili merilno linijo s protonskim žarkom v zraku. Protoni smo pospešili do ener-
kovanima, da bi tako odkrili morebitne posrebnine v pokosi-trenja. Ker z metodo PIXE ne moremo meriti lahkih elemen-
tov (kisika, ogljika, vodika), smo privzeli, da so kovine vezane
v izbrane kemične spojine, katerih skupni delež je prav tako
ena. Za biker smo privzeli, da je vezan v malahit CuCO3.Cu(OH)2,
za druge kovine pa smo predpostavili oksidno obliko. Tipični
delež kovin v taki korozijski plast je okrog 60 %. Za kovinsko
komponento smo nato preračunali še relativev deleže, tako da
smo vsoto kovinskih koncentracij normalirali na 100 %. Tako
dobljene vrednosti so se le za nekaj osebnih razlikovali 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 mm2
škušali čimbolj odstraniti korozijsko plast do kovinskega jedra,
in 2) korodirano površino fibul, kjer smo skusali odkriti mo-
rebitne sledi nanoza na prvotni površini (npr. posrebnitev, pokosi-
štenje itd.; prim. npr. Šmit 2003; Istenič, Milić, Šmit 2003,
291-292). Rezultate meritev na korodiranih mestih smo
v prvi vrsti pravo tako zamenjali na dva načina: 1) vsebnost posamez-
nih kovinskih elementov, ki smo jih izračunali kot sestavni del
kozijskih elementov, ki smo jih izračunali kot sestavni del
karbonatov in oksidov (v tabeli označeno z 'rca. za spojine'),
in 2) vsebnost posameznih kovinskih elementov, ki smo jih
dobili z normiranjem vrednosti kovin v spojih na 100 %
(označeno z 'norm. kovine').
Z meritvami mesti, s katerimi smo odstranili korozijsko in
tanko vhrnjo kovinsko plast, smo ugotavljali približno sestavo kovin-
skega jedra fibul. Pregled takoj pripravljene točke je pokazal, da je izredno težko povsem odstraniti korozijsko
plast odstranjena (cf. Istenič 2005, št. 1). Omenjeno korozijsko
plast je verjetno povzrocilo nanos kalcijevega polisulfitida, ki pa ga
meritev ni zaznala, ker nismo merili elementov, lažjih od železa.

št. 1 (tabl. 1)

Komentar:
Na mestih 1 in 2 (na spodnji strani loka) je bila odstranje-
na glavnina korozijskega splošnega površinskega površine.
Rezultati meritev kažejo, da je bila fibula izdelana iz
medene z najmanj okoli 20 % cinka. Meritve na
mesti 3 in 4 sta bili izmerjeni na zgornji strani loka na površi-
ni fibule, ne bi da bi odstranili korozijsko
plast odstranjena (cf. Istenič 2005, št. 1). Omenjeno korozijsko
plast je verjetno povzrocilo nanos kalijevega polisulfitida, ki pa ga
meritev ni zaznala, ker nismo merili elementov, lažjih od železa.

št. 2 (tabl. 2)

Komentar:

Na mestih 1 in 2 je bila odstranjena glavnina korozijskega splošnega
površine na površini fibule, na zgornji strani loka.

Rezultati meritev kažejo, da je bila fibula izdelana iz
dažna korozijskega splošnega površine.

št. 3 (tabl. 3)

Komentar:
Na mestih 1 in 2 je bila odstranjena glavnina korozijskega splošnega
površine, na površini na površini fibule.

št. 4 (tabl. 4)

Komentar:
Na mestih 1 in 2 je bila odstranjena glavnina korozijskega splošnega
površine, na površini na površini fibule.

št. 5 (tabl. 5)

Komentar:
Na mestih 1 in 2 je bila odstranjena glavnina korozijskega splošnega
površine, na površini na površini fibule.

Največja globina, do katere lahko izmeritmo profil, je odvisna od dosegeta protonov pri največji energiji in je običajno manjša od 10 µm. Na površini fibule št. 12 je tenka
plast korozijske, ki ni nastala na prvotni površini (prim. Istenič
2005). Koncentracija cinkovega jedra korozijskega površine je približno 1 %
in proti notranjosti počasi narašča (sl. 1).

Rezultati meritev so podani v preglednicah. Navedli smo le
železo, ki je po merjenih rezultatih najbolj vodilna v merjenih

Št. 1 (tabl. 1)

Komentar:
Na mestih 1 in 2 (na spodnji strani loka) je bila odstranje-
na glavnina korozijskega splošnega površine.

Rezultati meritev kažejo, da je bila fibula izdelana iz
medene z najmanj okoli 20 % cinka. Meritve na
mesti 3 in 4 le malo odstopajo od meritve na mestih 1 in 2, kar
potrjuje, da je bila odstranjena korozijska plast
odstranjena (cf. Istenič 2005, št. 1). Omenjeno korozijsko
plast je verjetno povzrocilo nanos kalijevega polisulfitida, ki pa ga
meritev ni zaznala, ker nismo merili elementov, lažjih od železa.

št. 2 (tabl. 2)

Komentar:
Na mestih 1 in 2 je bila odstranjena glavnina korozijskega splošnega
površine na površini fibule, na zgornji strani loka.

Rezultati meritev kažejo, da je bila fibula izdelana iz mede-
ne z najmanj okoli 21 % cinka. Na površini je bil nanos
druge kovine.

št. 3 (tabl. 3)

Komentar:
Na mestih 1 in 2 je bila odstranjena glavnina korozijskega splošnega
površine, na površini na površini fibule.

št. 4 (tabl. 4)

Komentar:
Na mestih 1 in 2 je bila odstranjena glavnina korozijskega splošnega
površine, na površini na površini fibule.

št. 5 (tabl. 5)

Komentar:
Na mestih 1 in 2 je bila odstranjena glavnina korozijskega splošnega
površine, na površini na površini fibule.
odstranjevanju korozije z merjene točke, sklepamo, da znana vsebnost kositir v jedru fibule manj kot 13 %.

V koroziji, ki je nastala na prvotni površini, je bil izmerjen visok delež kositira (mesto 1), kar bi lahko bila posledica pokositrenja ali pa korozijskih procesov (cf. Meeks 1993). Pre

gled 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 odstranjenja, nja

na površina ima rjavorodčevski sijaj. Točka 1 je majhna, zato je bila merjena tudi z ožkim žarkom. Mesto 2 je po drugi osesti odstraniti korozijo veliko, vendar pa so na njem drobne jamice, v katerih je korozija. Mesto 3 predstavlja korozijo na prvotni površini zgorne strani loka fibule.

Rezultati meritev mesta 2 kažejo, da je bila fibula izdelana iz bakrove zlitine, ki vsebuje okoli 20 % cinka. Na površini fibule ni bilo prevleke.

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 mesta 2 kažejo, da je bila fibula izdelana iz bakrove zlitine, ki vsebuje okoli 20 % cinka. Na površini fibule ni bilo prevleke.

Št. 11 (tab. 11)

Komentar:

Točki 1 in 2 sta bili izbrani na različno dobro ohranjeni sotočni srebrni plast na zgornji strani loka fibule. Na mestih 3 (na nogi), 5 in 6 (na spodnji strani loka fibule) je bila odstranjena korozija pod rumeno se svetleče kovinskega jedra.

Rezultati meritev kažejo, da je bila fibula izdelana iz medenine, ki vsebuje okoli 21 % cinka. Vsako delež kositira na mestih 1 in 2 kaže, da je bila fibula pokositrena.

Rezultati meritev kažejo, da je bila fibula narejena iz medenine, ki vsebuje okoli 21 % cinka. Vsako delež kositira na mestih 1 in 2 kaže, da je bila fibula pokositrena.

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 svetleče kovinskega jedra. Mesto 3 je po zadnjem odstranjevanju korozije najbolj očiščeno. Mesto 4 leži na ostanek twittera. Mesto 3 je bilo izbrano na zgornji strani loka fibule, kjer je bila prekrila korozijska plast do rumeno se svetleče kovinskega jedra. Mesto 4 leži na ostanek twittera.

Komentar:

Mesto 2 je bilo izbrano na kvoralne razširitve, ki je bila zelo tenka - mesto se kovinsko sveti.

Tanka srebrno se svetleče plast na površini zgorne strani fibule smo merili na mesto 1, kjer je razmeroma dobro ohranjen, in na mesto 2, kjer je slabi ohranjen. Na mestih 3 in 5 je bila odstranjena glavnina korozije, zato je vidno rjavorodčevski srebrni jedro.

Rezultati meritev mesta 2 kažejo, da je bila fibula narejena iz bakrove zlitine, ki je vsebovala najmanj okoli 7 % kositra, obokoli 5 % svinca. Koncentracija cinka je okoli 2-3 % v kovinsku jedro.

Št. 7 (tab. 7)

Komentar:

Mesto 1 je bilo izbrano na različno dobro ohranjeni sotočni srebrni plast na zgornji strani fibule. Na sprednji strani loka fibule, na kjer je verjetno nastala na prvotni površini fibule.

Rezultati meritev mesta 2 kažejo, da je bila fibula izdelana iz bakrove zlitine, ki je vsebovala najmanj okoli 7 % cinka. Na površini fibule ni bilo prevleke.

Rezultati meritev mesta 2 kažejo, da je bila fibula izdelana iz bakrove zlitine, ki je vsebovala najmanj okoli 7 % cinka. Na površini fibule ni bilo prevleke.

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 svetleče kovinskega jedra. Mesto 1 je bilo odstranjeno z večkrat merjenjem mest 4 ali pa je bila fibula izdelana iz bakrove zlitine, ki je vsebovala najmanj okoli 7 % cinka. Koncentracija cinka je okoli 2-3 % v kovinsku jedro.

Mesto 1 je bilo izbrano na različno dobro ohranjeni sotočni srebrni plast na zgornji strani fibule.

Rezultati meritev mesta 2 kažejo, da je bila fibula narejena iz bakrove zlitine, ki je vsebovala najmanj okoli 7 % cinka. Na površini fibule ni bilo prevleke.

Rezultati meritev mesta 2 kažejo, da je bila fibula izdelana iz bakrove zlitine.

Št. 9 (tab. 9)

Komentar:

Na mestu 1, izbranem na spodnji strani loka fibule, je bila odstranjena glavnina korozije do rumeno se svetleče kovinskega jedra. Mesto 2 je bilo izbrano na korozijskih deformacijh na sprednji strani loka fibule.

Rezultati meritev mesta 2 kažejo, da je bila fibula izdelana iz bakrove zlitine, ki vsebovala najmanj okoli 7 % cinka. Koncentracija cinka je okoli 2-3 % v kovinsko jedro.

Mesto 1 je bilo izbrano na različno dobro ohranjeni sotočni srebrni plast na zgornji strani fibule.

Rezultati meritev mesta 2 kažejo, da je bila fibula narejena iz bakrove zlitine.

Št. 10 (tab. 10)

Komentar:

Na mestih 1 in 2 (izbranih na spodnji strani loka fibule) je bila odstranjena glavnina korozije do rumeno se svetleče kovinskega jedra: obe mesti sta bili merjeni večkrat. Mesto 1 je večje in bolje očiščeno. Mesto 3 (na spodnji strani loka fibule) je bila odstranjena korozijska plast do rumeno se svetleče kovinskega jedra.

Rezultati meritev kažejo, da je bila fibula izdelana iz medenine, ki vsebuje okoli 21 % cinka. Vsako delež kositira na mestih 1 in 2 kaže, da je bila fibula pokositrena.

Št. 13 (tab. 13)

Komentar:

Na mestu 1 je bila odstranjena glavnina korozije do rumeno se svetleče kovinskega jedra. Na zgornji strani je bila odstraniti korozijska plast do rumeno se svetleče kovinskega jedra. Mesto 3 sta bili izbrani na korozijskih deformacijh.

Rezultati meritev mesta 2 kažejo, da je bila fibula izdelana iz bakrove zlitine, ki vsebovala najmanj okoli 7 % cinka. Koncentracija cinka je okoli 2-3 % v kovinsko jedro.

Mesto 1 je bilo izbrano na različno dobro ohranjeni sotočni srebrni plast na zgornji strani fibule.
št. 15 (tab. 15)
Komentar:
Na mestih 1 in 2, ki smo ju izbrali na spodnji strani loka fibule, smo odstranili glavno korozijsko živo. Mesto 1 je razmeroma veliko in dobro očiščeno. Na obeh mestih je vidna kovinsko se svetleča rumena površina. Mesti 3 in 4 predstavljata korozijsko predel, prikazan na mestu 4 je dobro ohranjena korozijska območja.

Rezultati meritev so pokazali, da je bila fibula izdelana iz medene in 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 glavno korozijsko živo; 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 korozijski območju, mesto 3 pa na ovalni razširitvi loka, kjer je korozijska živa jamečasta.

Rezultati meritev kažejo, da je bila fibula izdelana iz medene in najmanj okoli 16 % 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 glavno korozijsko živo. Na očiščenem delu je vidna kovinsko se svetleča rumena površina, na kateri pa so še vidni ostanek korozijske žive. Zaradi izredno slabe ohranjenosti fibule ni bilo mogoče pripraviti mesta, s katerega bi odstranili vso korozijsko plast. Iz istega razloga tudi nismo merili korozijsko ohranjenost.

Rezultati meritev kažijo, da so bili na merjenem mestu ostatki korozijske žive, kažejo, da je bila fibula izdelana iz medene in najmanj okoli 16 % cinka, ki je verjetno vseboval faze 

št. 18 (tab. 18)
Komentar:
Na mestu 2 (na spodnji strani loka fibule) smo odstranili glavno korozijsko živo; vidna je rumena se svetleča površina. Mesti 3 in 4 sta bili izbrani na korozijskem delu z ohranjeno korozijsko živo. Na mestih 3 in 4 sta bili izbrani na korozijskih prehranah, v katerih je prisotna voda ali vlaga. Pri agresivnejših korozijskih območjih se pojavlja predvsem bakrov oksid. Pokositrenje ohranja zelo stabilen kositrov okvir.

Opisana korozijska degradacija se pojavlja v običajnem okolju, kjer je prisotna voda ali vlaga. Pri agresivnih korozijskih območjih se pojavlja predvsem bakrov oksid.

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

Vrstični elektronski mikroskop (SEM) omogoča preiskovanje površin in optičnih faz. SEM omogoča prikazati toplotne oblike in korozijsko znanost.

Vrstična elektronska mikroskopija (SEM) omogoča prikazati toplotne oblike in korozijsko znanost.

št. 5
Komentar:
Fibula št. 5 na površini kaže očitne znake pokositrenja. Analize SEM EDX so pokazale, da je bila izdelana iz brona z okoli 10 % Sn. Pri pregledovanju so bili v nobenem občutljivih območjih znaki pokositrenja.

št. 6
Komentar:
Na primjerjevju smejo zvrstati v red: (Cu3Sn), ki nastane pri segrevanju na teploto okrog 350 °C in vsebuje 38,2 % kositra. 

št. 7
Komentar:
Na mestih 1 in 2, ki smo ju izbrali na spodnji strani loka fibule, smo odstranili glavno korozijsko živo; vidna je rumena se svetleča površina. Mesti 3 in 4 sta bili izbrani na korozijskih prehranah.

št. 8
Komentar:
Na mestu 2 (na spodnji strani loka fibule) smo odstranili glavno korozijsko živo; vidna je rumena se svetleča površina. Mesti 3 in 4 sta bili izbrani na korozijskih prehranah.

št. 9
Komentar:
Na mestih 1 in 2, ki smo ju izbrali na spodnji strani loka fibule, smo odstranili glavno korozijsko živo; vidna je rumena se svetleča površina. Mesti 3 in 4 sta bili izbrani na korozijskih prehranah.

št. 10
Komentar:
Na mestih 1 in 2, ki smo ju izbrali na spodnji strani loka fibule, smo odstranili glavno korozijsko živo; vidna je rumena se svetleča površina. Mesti 3 in 4 sta bili izbrani na korozijskih prehranah.
nastih. Ena fibula je narejena iz rdeče litine, tj. zlitine bakra s kositrom in cinkom (št. 3), in tri iz bronastih fibul (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 korozija plasti 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 cinku nismo zaznali.

Meritve korozije na medenini s tehniko PIXE so prav tako pokazale razmeroma majhne delež cinka. Na mestih, s katereh 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 povisan delež kositra lahko več vzrokov. Preiskava s vrstičnim elektronskim mikroskopom so pokazale, da pri fibuli št. 5 povisšan delež kositra verjetno ni posledica pokostišenja.