Analysis of copper-alloy fitments on a Roman *gladius* from the river Ljubljanica

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Izvleček

Z metodo protonsko vzbujenih rentgenskih žarkov (PIXE) smo določili sestavo bakrovih zlitin na nožnici rimskega meča, ki je bil najden v strugi Ljubljanice. Nožnično okovje je narejeno iz medenine, le majhni deli podlage v obliki črke U so iz brona. Posamezni sestavni deli okovja so spojeni s kovičenjem in spajkanjem, pri čemer so uporabili kositrno-svinčev lot. Rezultati analize potrjujejo rabo medenine v zgodnjem avgustejskem obdobju. Zanesljivost dobljenih rezultatov smo ocenili z modeliranjem.

Abstract

The method of proton induced X-ray emission (PIXE) analysis was applied for studies of the metal composition of copper-based alloys on the scabbard of a Roman *gladius*, discovered in the river Ljubljanica. The scabbard fitments were made of brass, except for small parts of the U-shaped lining made of bronze. The fitting components were bound by riveting and soldering using a tin-lead alloy. The analysis testifies to the use of brass in the early Augustan era. The reliability of the PIXE results is discussed.

PRINCIPLES OF THE METHOD

The method of PIXE requires irradiation of the investigated sample by an ion beam. The impact of energetic projectiles produces vacancies in deep inner shells of the target atoms. Filling of these vacancies from the outer shells may result in the emission of energetic photons in the X-ray energy region. The photon energies depend on the emitting atom and enable easy identification of the target constituents. The method is not sensitive to light elements (lighter than approximately sodium) since they emit photons with energies too low to be detected. The measured X-ray intensities are related to the concentrations of the target elements. This relation is linear only in specially prepared thin targets where the projectiles loose a negligible amount of their energy. For the analysis of precious objets it is desirable to impair the object to the smallest possible extent, avoiding any sampling procedure. The analysis is performed at selected points representative of the whole object. As the projectile ions now stop in the object completely, the relation between the measured X-ray intensities and elemental concentrations depends on several processes which have to be properly modeled in the concentration evaluation algorithms.

Along their path, the particles gradually loose their energy and thus the ability to ionize atoms. In order to take this effect into account, it is necessary to know the energy dependence of the X-ray production cross-section and the stopping power of the target material. The X-rays produced in the irradiated volume penetrate some of the target material before reaching the detector, so they are partially absorbed in the target itself. The absorption effect can be estimated by knowing the X-ray attenuation coefficient of the target material, and the geometrical paths of the X-rays. These are conveniently modeled for a well defined experimental geometry only - a smooth plane surface of the target is regularly assumed. An uneven target surface usually increases the paths of X-rays and thus reduces the X-ray yields. The X-ray yields also contain a contribution from the secondary processes, importantly by the X-ray fluorescence induced by the more energetic X-ray yields in the sample itself.

The unknown concentrations are determined by an iterative procedure, as the calculations of the

projectile stopping and X-ray absorption effects depend on the target composition. The algorithm is largely simplified for the case of metal targets composed of elements which all emit detectable X-rays. The requirement that the sum of all constituents equals 100% implies that the concentrations depend only on the ratios of the measured X-ray yields. The evaluated concentrations are not sensitive to the uncertainty of the stopping powers, which is typically 10%.

For the present analysis, protons of 2.03 MeV nominal energy were used. The proton beam was extracted into air through an 8 μm aluminum foil. Before hitting the object, it passed an air gap approximately 1 cm thick; so that the object impact energy was then approximately 1.6 MeV. The X-rays were detected by a Si(Li) semiconductor detector placed at 45^0 with respect to the beam at a distance of 60 mm. The detector was shielded with layers of kapton foil totally 0.75 mm thick in order to reduce the counting rate of soft X-rays. The concentrations were evaluated according to a method[1] which takes into account the thick target effects described above. The analysis of experimental errors is given in Sec. 3.

CHOICE OF MEASURING POINTS AND EXPERIMENTAL RESULTS

The analysis attempted to identify all copper-based alloys used for the scabbard fittings. For measurements, 24 characteristic points were selected on smooth and plane parts of the fittings[2] (*Fig. 1*). In addition to the cleaning and restoration procedure[3], the points were gently polished using a rotating rubber polisher over an area of about 3 mm^2. The protons of about 1.6 MeV impact energy were collimated to a beam spot size of about 1 mm^2. The proton current was several nA, and the measuring time was about 10 minutes per point. The statistical uncertainties were below 1% for Cu and Zn, but they amounted up to 30% for Sn which was present in concentrations smaller than 1%. The collected spectra were treated by the AXIL program[4], and the elemental concentrations were calculated by a previously described program[1,5].

Analyzed point	Fe	Cu	Zn	Pb	Sn
1	1.78	7.3	0.43	21.2	69.2
2	1.21	88.0	-	1.0	9.8
3	1.16	86.8	-	1.2	10.8
4	0.57	77.3	20.4	0.3	1.3
5	0.29	82.5	15.5	0.7	1.0
6	0.37	78.9	19.3	0.1	1.3
7	1.09	79.5	16.9	0.5	1.9
8	3.2	14.0	1.5	26.3	55.0
9	0.35	83.4	15.2	0.1	0.9
10	0.29	82.2	16.5	0.1	0.9
11	0.68	72.7	-	1.31	25.3
12	8.6	4.1	0.4	11.9	75.0
13	0.31	79.1	19.9	0.4	0.3
14	0.52	80.8	17.2	0.8	0.6
15	0.63	81.0	16.8	0.2	1.4
16	0.75	79.7	18.1	0.2	1.2
17	0.82	93.7	-	0.1	5.3
18	0.38	79.7	18.6	0.9	0.4
19	0.46	84.3	14.9	0.04	0.3
20	1.14	82.9	14.9	0.1	0.9
21	0.49	80.2	18.5	0.1	0.7
22	0.61	77.6	20.7	0.2	0.8
23	0.47	78.4	20.0	0.2	0.9
24	1.8	79.1	18.2	0.2	0.7

Table 1: Elemental concentrations (in weight%) determined at the points marked in *fig.1*.
Tab. 1: Koncentracije elementov (v utežnih %), ki smo jih določili na mestih, označenih na *sl. 1*.

The results are shown in *table 1*. The scabbard binding was made of brass which contains about 18% of Zn (points 4-7, 9, 10, 13-16, 19-24). It consists of five parts[2] which were soldered to the U-shaped lining. The composition of the lining was determined at three points (2, 3, 17). The content of Sn at the outer points 2, 3 was about 10%, and in the inner point 17 about 5%. It is possible that the points 2, 3 - which lie on the exposed convex surface - were contaminated by Sn during the soldering process. The lower content of about 5% Sn then appears more reliable since it was obtained on the concave surface far from the soldering region.

For soldering of the binding, a tin-lead alloy was used (1, 11, 12). Soldering was also applied to reinforce the riveting on the net-like fitment (8). The composition of the solder varied at the points measured. The small soldering junctions allowed

[1] Ž. Šmit, M. Budnar, V. Cindro, P. Kump, V. Ramšak, M. Ravnikar, *Nucl. Instr. Meth. Phys. Res.* B49, 1990, 157.
[2] J. Istenič, in this volume.
[3] S. Perovšek, Z. Milić, in this volume.
[4] P. Van Espen, H. Nullens, F. Adams, *Nucl. Instr. Meth*. 145, 1977, 579.
[5] Ž. Šmit, *Nucl. Instr. Meth. Phys. Res*. B17, 1986, 156.

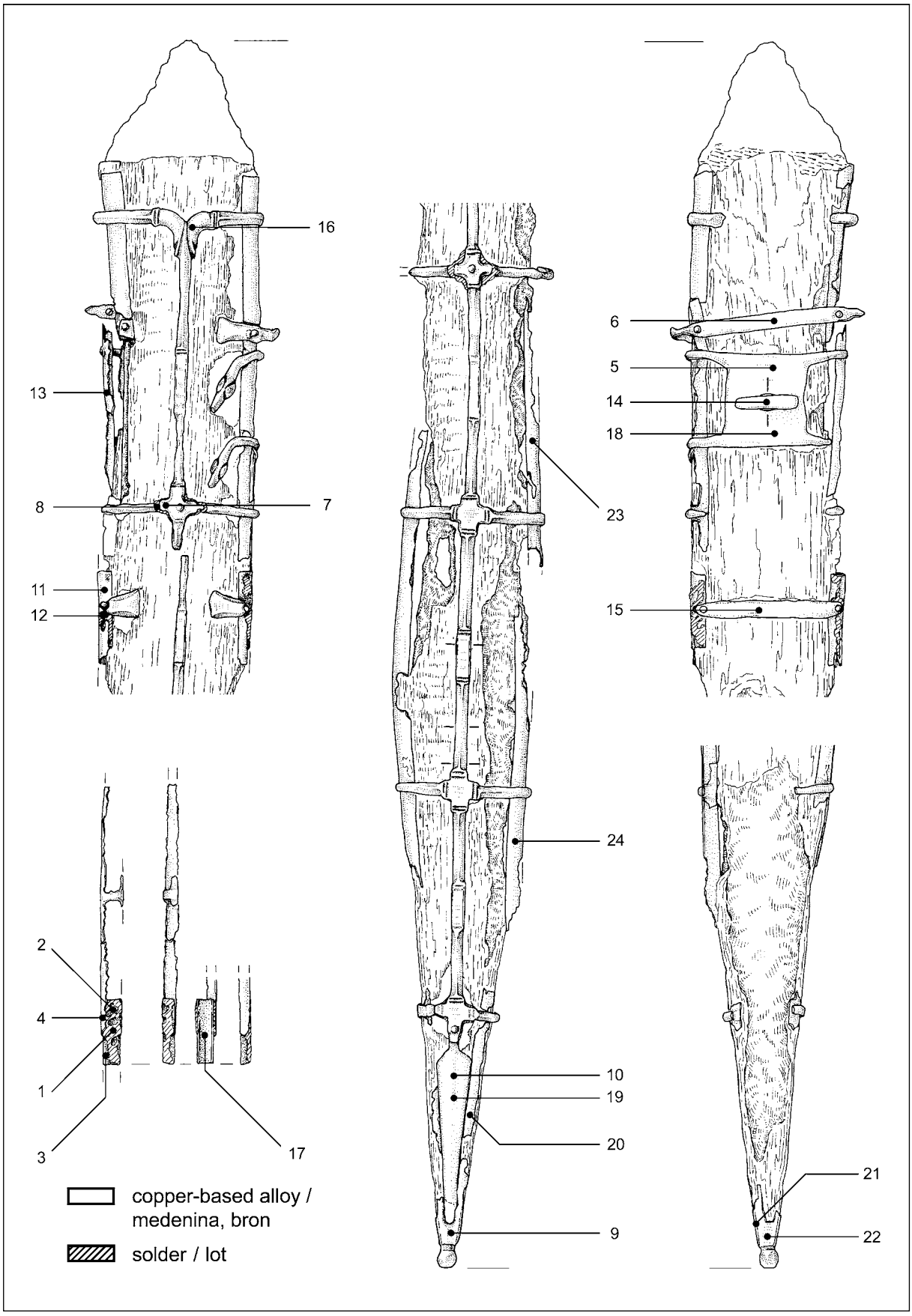

Fig. 1: Selection of measuring points on the scabbard binding and lining.
Sl. 1: Izbor merskih točk na nožničnem okovu in podlogi.

an area of only about 1mm^2 to be hit by the proton beam, so it was then probable that the protons also hit the neighbouring material. This may also explain a large content of iron at point 12.

DISCUSSION

The content of zinc in the brass points varies from 15 to 21%. The source of this variation is important - whether it reflects inhomogeniety of the material or is brought about by the uncertainty of the measuring method. A detailed study of error propagation was made by numerical simulation. A set of numerical X-ray yields was generated, reproducing the brass alloy with a model concentration of 20% Zn and 1% Fe. The variation of these two concentrations was then followed according to variations in the experimental parameters which may occur during actual measurements, such as changing the proton impact energy by 50 keV, tilting the sample by 10^0, and changing the air-path of the X-rays by 1 cm (*Table 2*). We also estimated the influence of the random surface roughness of 0.005 g/cm^2 (approximately corresponding to 5 μm).[6] *Table 1* shows a much smaller variation of Zn and Fe than observed experimentally, so we may conclude that the measurements demonstrate local concentration variations. These may be characteristic for the material itself having their origin in the production process[2], or may result due to the selective leaching during the burial period. Zinc, having lower electrode potential than copper, was non-uniformly leached out of the alloy. The effect of leaching is clearly observed in the uneven and pitted surface around the points 19, 20, which exhibit the lowest zinc content.

The evaluated concentrations also contain a systematic error which depends on the uncertainty of the physical parameter data base, the detector efficiency, and the thickness of the kapton absorber. The uncertainty of the detector efficiency is less important for the analysis of brass, as the energies of copper and zinc X-rays are very close, while the effect of increasing the absorber thickness by 30 μm is shown in *table 2*. We may conclude that the zinc concentrations are systematically uncertain by 5%, while the random error is below 1%. The variation of the iron concentration in the model brass implies random errors of about 5%; we may then assume the total uncertainty of the iron content is within 10%.

	Zn	Fe	Sn
Nominal concentrations (%)	20	1	10
Energy increased by 50 keV	19.94	1.01	9.67
Sample tilted by 10^0	19.87	1.04	9.66
Air gap increased by 1 cm	19.97	1.01	9.91
Surface roughness 0.005 g/cm^2	19.73	1.06	9.27
Kapton absorber 30 μm thicker	19.92	1.02	9.81

Table 2: Propagation of experimental uncertainties, obtained by model calculation on a hypothetical brass (20% Zn, 1% Fe) and bronze (10% Sn) samples. The variation of calculated concentrations is shown as a function of the variation of experimental parameters.
Tab. 2: Vzroki za eksperimentalne napake, kot smo jih ocenili z modelnim računom za namišljena vzorca medenine (20 % Zn, 1 % Fe) in brona (10 % Sn). Različne koncentracije smo izračunali tako, da smo spreminjali vrednosti količin, ki vplivajo na izid meritev.

A similar numerical study was made for a model bronze containing 10% Sn (*Table 2*). The concentration variation is 5%. The Sn concentration in bronze is then uncertain by 10%, provided the detector efficiency is known to within several percent. Test measurements were performed on a modern brass, containing 37% Zn, and on a tin-lead solder, containing 60% Sn. The relative differences between the measured and nominal concentrations were within 5%.

In certain samples, the concentrations may vary with the sample thickness. This effect can be observed experimentally by reducing the proton impact energy or by tilting the sample, thus producing characteristic X-rays closer to the surface. Markedly different X-ray intensities originating from different target depths reveal the concentration gradient. The method, which proved useful for the analysis of gold items[7], was not applied in the present case as the analyzed surfaces were not smooth enough.

Summarizing the data on brass points, the mean Zn content is given by 17.7 ±2.0%, and the mean Fe content by 0.62±0.39%. The variations of the two elements exhibit variations of concentrations at different parts of the surface. An inspection of the inner parts would require removal of a more target material. The mean content of Pb is 0.30±0.27%, and the mean content of Sn is 0.9±0.4%. The variation of these two elements is mainly due to the statistical variation of X-ray yields. The mean content of Sn is expected to be about 1%; this value nevertheless appears a little high for an impurity from the ore.

[6] J. L. Cambell, R. D. Lamb, R. G. Leigh, B. G. Nickel, J. A. Cookson, *Nucl. Instr. Meth. Phys. Res*. B12, 1985, 402; Ž. Šmit, *Nucl. Instr. Meth. Phys. Res*. B28, 1987, 567.

[7] G. Demortier, *Nucl. Instr. Meth. Phys. Res*. B113, 1996, 347.

The scabbard fitments were then made of a relatively pure brass. As the *gladius* represents a datable object, the brass fitments provide important evidence for the early use of brass at the beginning of the second half of the first century B.C. [2]

CONCLUSION

The method of PIXE using an external proton beam was successfully applied for the characterization of copper-based alloys on the scabbard of a Roman *gladius*. The advantage of surface analysis is its non-destructiveness, especially when the sample consists of a thin metal sheath. The reliability of the analysis can be increased by a more radical exposure of the material inside. However, it is the decision of the object curator whether such information is worth the damage to the object. The present results provide useful information on the major types of alloys, notably on the use of brass.

Analize bakrovih zlitin na nožnici rimskega meča iz Ljubljanice

Povzetek

Z metodo PIXE[1] smo analizirali okovje na nožnici rimskega meča iz struge Ljubljanice.[2] Analiza temelji na obsevanju vzorca z žarkom visokoenergijskih ionov, ki v atomih vzorca ustvarijo vrzeli. Pri zapolnitvi vrzeli se izsevajo rentgenski žarki z energijami, ki so značilne za posamezne elemente. Iz rentgenskega spektra tako razberemo, kateri elementi sestavljajo vzorec. Z upoštevanjem vseh pojavov, ki vplivajo na število rentgenskih žarkov (ustavljanje ionov v snovi, absorpcija rent-genskih žarkov v vzorcu in v drugih absorberjih, fluorescence zaradi tršihrentgenskih žarkov) lahko izračunamo tudi koncentracije elementov v vzorcu.[1,5] Metoda je nedestruktiv-na, ker lahko analizo opravimo v izbranih točkah in situ brez odvzemanja vzorčnega materiala. Nabiti delci prodrejo v pred-met le nekaj stotink milimetra globoko, tako da je analiza omejena na tanko površinsko plast. Na nožnici rimskega meča smo v glavnem analizirali okov iz tanke pločevine, kjer bi odvzemanje materiala povzročilo precejšno škodo, ponekod pa sploh ne bi bilo mogoče. Izbrana merska mesta smo očistili s poliranjem,[3] s čimer smo odstranili površinske okside. Meritev smo opravili s protonskim žarkom energije 2 MeV v zraku.

Rezultati (*tab. 1*) kažejo, da je okovje na nožnici skoraj v celoti narejeno iz medenine z okoli 18 % cinka (točke 4-7, 9, 10, 13-16, 18-24), le drobni deli podlage v obliki črke U so iz brona. Podlago smo analizirali v treh točkah. Koncentracija kositra na zunanji strani (2, 3) je bila okrog 10 %, na notranji strani (17) pa okrog 5 %. Manjša vrednost je zanesljivejša, ker so na zunanji strani sledovi lota, zaradi česar je verjetno prišlo do površinskega onesnaženja podlage s kositrom. Okovje je na podlago prispajkano s kositrno-svinčevim lotom (1, 11, 12). Z lotom so okrepili tudi kovnične zveze na mrežastem okovu (8). Koncentracije elementov v posameznih točkah lota se precej spreminjajo, verjetno zato, ker je bila za meritev na razpolago le majhna površina lota, protonski žarek pa je deloma zadel tudi okolico.

Koncentracija cinka na različnih mestih medeninastega okovja niha med 15 in 21 %. Kot smo se prepričali z modelom (*tab. 2*), tako spreminjanje koncentracij ni posledica slučajnih eks-perimentalnih napak. Medenina je lahko nehomogena zaradi samega proizvodnega postopka,[2] lahko pa se je cink neenakomerno izlužil s površine, saj ima manjši elektrodni potencial kot baker. Sestavo zlitine globlje pod površino bi lahko otipali le tako, da bi odstranili debelejšo površinsko plast. Kljub širokemu razponu izmerjenih koncentracij je določitev medenine kot materiala nedvomna in služi kot pomemben dokaz za njeno rabo v zgodnjem avgustejskem obdobju.[2]

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